

PALAEOPIGMENT ACCUMULATION AND IMPLICATIONS FOR  
PALEOLIMNOLOGY OVER THE LAST CENTURY FOR TWO ONTARIO LAKES

By

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A THESIS

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## Abstract

Crawford Lake is a meromictic lake, which is 24 m deep and has an area of 2.5 ha, and has never been reported to have mixed below 16 m. Lady Evelyn Lake, which became a reservoir when a dam was built in 1916, is dimictic with a maximum depth of about 35 m.

My research proved that both native chlorophylls and the ratio of chlorophyll derivatives to total carotenoids were better preserved in the shallower lake (Crawford Lake) because it was meromictic. Thus the anaerobic conditions in Crawford Lake below 16 m (monimolimnion) provide excellent conditions for pigment preservation. Under such conditions, the preservation of both chlorophylls and carotenoids, including oscillaxanthin and myxoxanthophyll, are extremely good compared with those of Lady Evelyn Reservoir, in which anaerobic conditions are rarely encountered at the mud-water interface.

During the period from 1500 to 1900 A. D. in Crawford Lake, the accumulation rates of oscillaxanthin and myxoxanthophyll were extremely high, but those of chlorophyll derivatives and total carotenoids were relatively low. This was correlated with the presence of a dense benthic mat of cyanobacteria near the lake's chemocline. Competition for light between the deep dwelling cyanobacteria and overlying phytoplankton in this meromictic lake would have been intensified as the lake became more and more eutrophic (1955-1991 A. D.).

During the period from 1955 to 1991 A. D., the accumulation rates of chlorophyll derivatives and total carotenoids in the sediment core from Crawford Lake (0-7.5 cm, 1955-present) increased. During this same period, the accumulation rates of cyanobacterial pigments (i.e.

oscillaxanthin and myxoxanthophyll) declined as the lake became more eutrophic.

Because the major cyanobacteria in Crawford Lake are benthic mat forming *Lyngbya* and *Oscillatoria* and not phytoplankton, eutrophication resulted in a decline of the mat forming algal pigments. This is important because in previous palaeolimnological studies the concentrations of oscillaxanthin and myxoxanthophyll have been used as correlates with lake trophic levels.

The results of organic carbon  $\delta^{13}\text{C}$  analysis on the Crawford Lake sediment core supported the conclusions from the pigment study as noted above. High values of  $\delta^{13}\text{C}$  at the depth of 34-48 cm (1500-1760 A. D.) were related to a dense population of benthic *Oscillatoria* and *Lyngbya* living on the bottom of the lake during that period. The *Oscillatoria* and *Lyngbya* utilized the bicarbonate, which had a high  $\delta^{13}\text{C}$  value. Very low values were found at 0-7 cm in the Crawford sediment core. At this time phytoplankton was the main primary producer, which enriched  $^{12}\text{C}$  by photosynthetic assimilation.

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## Introduction

For more than 30 years limnologists and paleoecologists have been examining fossil pigments in the sediments of freshwater lakes (Vallentyne, 1954, 1956; Gorham, 1960, 1961; Fogg and Belcher, 1961; Sanger and Gorham, 1970, 1972; Sanger and Crowl, 1979; Swain, 1985). These researchers noted the universal presence of chlorophyll derivatives and carotenoids both in surface sediments and in older material from sediment cores. The greatest concentrations of chlorophyll derivatives and total carotenoids occurred in eutrophic lakes and lesser amounts occurred in oligotrophic lakes. This suggested the potential use of sedimentary chlorophyll degradation products (SCDP) as an index of lake productivity. Variations in preserved pigments from cores might therefore display a record of past trophic levels, since productive lakes have a greater fallout of pigmented detritus than oligotrophic lakes (Swain, 1985; Sanger, 1988).

Several factors influence the deposition and preservation of pigments. Changes of these factors over time have made the interpretation of paleopigment stratigraphies very difficult and ambiguous (Likens and Davis, 1975; Daley *et al.*, 1977; Huttunen and Tolonen, 1977; Tolonen, 1978). Interpretation of paleopigments depends on a clear understanding of the following factors:

Low oxygen concentrations in the water column and at the sediment surface during times of the year when productivity is high promotes pigment preservation (Carpenter and Berquist, 1985). If the basin depth is great enough for stratification to develop, the resuspension of sedimented materials is prevented and the pigments in the sediments can be well preserved. High sedimentation rates can

results in the rapid burial of the sedimenting detritus. This, too, prevents pigments from being destroyed (Swain, 1985).

Water temperature is important, especially in the deep profundal areas where detritus comes to rest. Cold bottom water conditions will tend to preserve pigments better than warm water conditions (Sanger, 1988).

Photochemical decomposition of pigments is well documented (Hertzberg *et al.*, 1971). Low light conditions throughout the water column serve to preserve pigments (*ibid*).

Extensive populations of detritus feeding benthics are of considerable importance. Passage of organic matter through the guts of Oligochaetes and larval Chironomidae can result in alteration of organic molecules (Brinkhurst and Jamieson, 1971).

The choice of reasonable sampling sites is critical to the reconstruction of the past environments from the fossil record. Clearly, meromictic lakes offer the best situation for pigment preservation, reducing problems of differential diagenesis of the pigments, and promoting comparability of measurements along the length of the core (Dickman, 1985). Dimictic lakes that stratify and maintain anoxic bottom water for much of the year constitute the next best option.

The main goal of this research was to investigate the relationship between the pigment accumulation and the long-term changes of lake environments for two Ontario lakes, a meromictic lake, Crawford Lake and a dimictic lake, Lady Evelyn Reservoir. Secondly, by comparing the paleopigments in the sediments in both of these lakes, I tried to evaluate the influence of several different factors, i.e. dissolved oxygen, light intensity, temperature and sedimentation rate, on pigment

preservation in their sediments. In order to determine the source of organic carbon in the sediments of Crawford Lake, I used the ratio of two stable isotopes, carbon-12 and carbon-13. This ratio and the ratio of native chlorophyll to chlorophyll derivatives and the ratio of chlorophyll derivatives to total carotenoids were used to assess pigment preservation levels in the sediment cores from both lakes.

## Lake Description

### *Crawford Lake*

Crawford Lake (Fig. 1) is located in Silurian Guelph-Anabel Dolomite on the top of the Niagara Escarpment 290 m above sea level about 70 km north of Toronto (latitude:  $45^{\circ} 36'$ , longitude:  $79^{\circ} 45'$ ; Dickman, 1985). Large white cedars (*Thuja occidentalis* L) ring the lake along its high cliffs preventing high winds from reaching the lake's surface (Boyko, 1978). As a result, the lake, which is 24 m deep and has an area of 2.5 ha (Fig. 2), has never mixed below 16 m (Dickman, 1985).

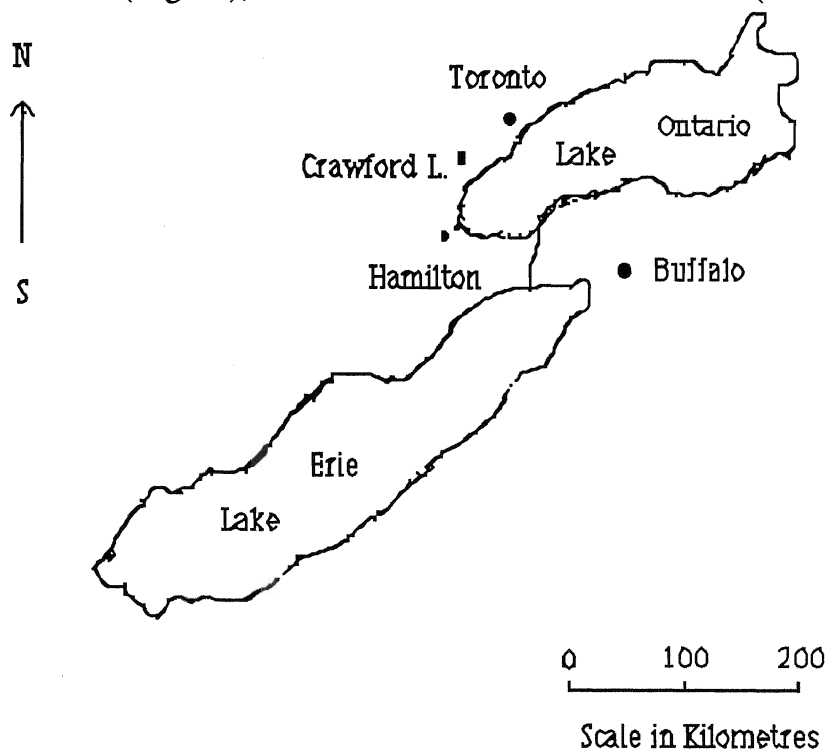


Fig. 1. The location of Crawford Lake

Meromictic lakes are rare and highly prized for unusual organisms, including phototrophic bacteria. In addition, their sediments are frequently varved, making them ideal systems for paleoecological studies (Ludlam, 1969). Because the varving pattern in these meromictic lakes is intimately linked to the frequency and intensity of chemocline ventilation (Dickman, 1985), it is extremely important to paleolimnologists to be able to distinguish between meromictic and oligomictic lakes.

The water in meromictic lakes does not mix completely each year because the stability of the water column is maintained by a chemically induced density gradient. Hutchinson (1957, p. 462) described oligomictic lakes as those which circulate (turnover) only at very rare (irregular) intervals while meromictic lakes were described as lakes in which "some water (i.e. the monimolimnion) remains permanently unmixed with the main water" (Ibid p. 480). The term "monimolimnion" was introduced by Findenegg in 1937 as described by Wetzel (1983), the same year that Hutchinson introduced the term "chemocline."

Crawford Lake, is one of the better known meromictic lakes in southern Ontario. To date, only 3 such lakes have been described for Quebec and less than two dozen have been described for New York and Ontario respectively (Anderson and Love, 1980).

### *Lady Evelyn Reservoir*

Lady Evelyn Reservoir is a dimictic mesotrophic lake in central Ontario near the Township of Barr, District of Timiskaming (latitude: N 44-53°, longitude: 78-74°; Fig. 3). Before 1916 A. D., the reservoir

## Crawford Lake

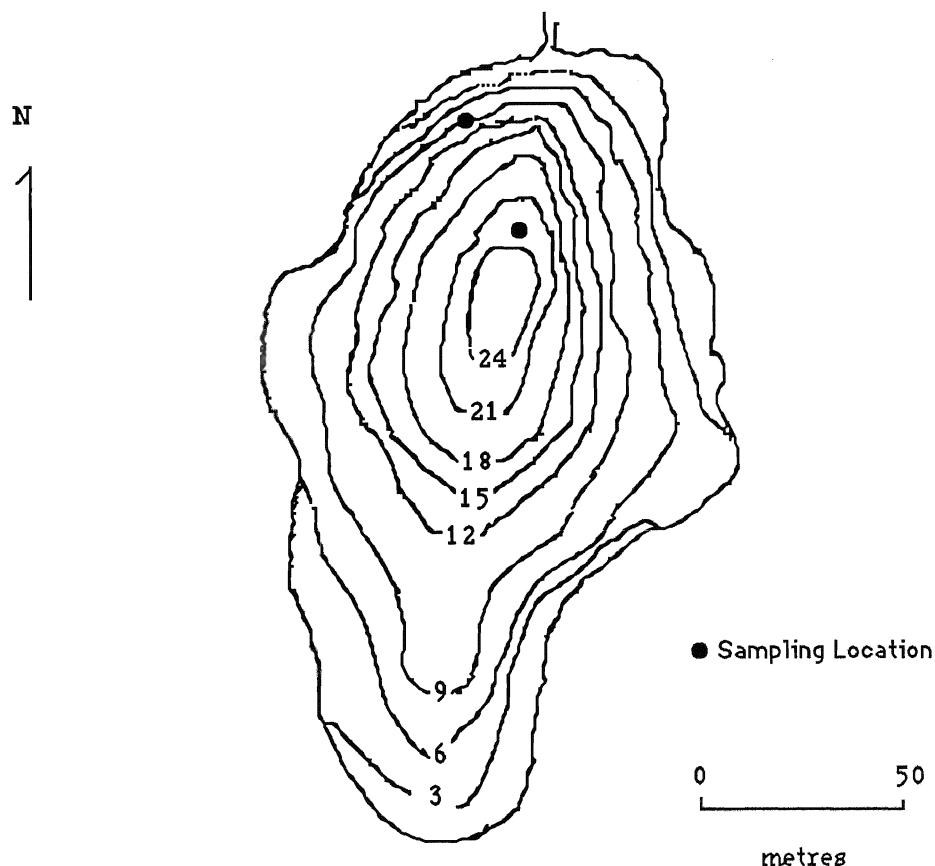


Fig. 2. Morphometric map of Crawford Lake

was a lake. In 1916, a dam was built on Lady Evelyn Lake. After that date, Lady Evelyn Lake became a reservoir (Lady Evelyn Reservoir). In 1976, a big concret dam was built on Lady Evelyn Reservoir. The reservoir was chosen in order to determine how algal pigments degrade over time in environments where dissolved oxygen, elevated temperature and low light were all present at the sediment-water interface.

Lady Evelyn Lake has a maximum level of El. 289.51 m and a nominal minimum of El. 284.38. Normally, the lake is only drawn down to El. 284.99 m each winter.



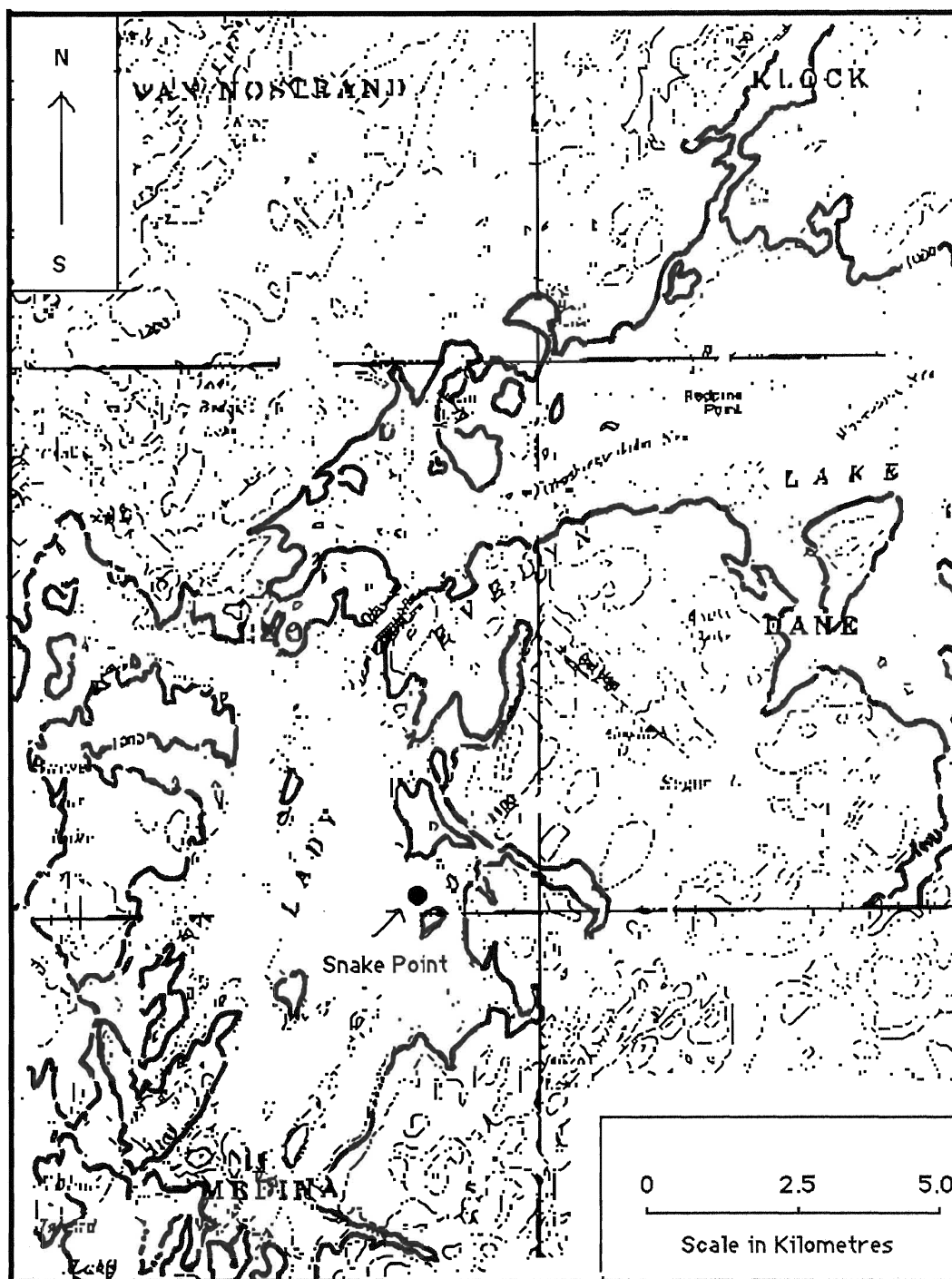


Fig. 3. Map of Lady Evelyn Reservoir, samples were taken from a depth of 30 m of water near Snake Point as indicated by the arrow.

## Chlorophylls and Carotenoids

### *Chlorophylls*

The fact that chlorophyll is one of the most important photoreactive pigments known to man scarcely requires emphasis (Allen *et al.*, 1960). This pigment is present in one or more forms in all organisms that carry out the fundamental reactions of transformation of light energy into chemical energy, without which life on this earth would be severely limited, if not impossible (Allen *et al.*, 1960).

The numerous varieties of photosynthetic organisms that exist have been very conservative in the pigments elaborated in their photoreactive organelles. Only a few kinds of chlorophyll are found in the living world. The most adventurous organisms appear to have been the bacteria. Photosynthetic purple bacteria contain a characteristic chlorophyll and the green bacteria contain at least two chlorophylls (Stanier, 1960). All the phyla of organisms that carry out green plant photosynthesis, i.e., reduction of carbon dioxide to sugars accompanied by the evolution of oxygen, contain the same green pigment, chlorophyll *a*. Sometimes this pigment is accompanied by one to three additional chlorophylls, *b*, *c*, and *d*. The distribution of these chlorophylls among the various groups of photosynthetic organisms is indicated in the following table (Table 1, Allen *et al.*, 1960).

Table 1. Distribution of chlorophylls in photosynthetic algal phyla (Allen *et al.*, 1960)

Group of organism	a	Chlorophyll		
		b	c	d
Cyanophyta	+	-	-	-
Rhodophyta	+	-	-	±
Chrysophyta				
Chrysophyceae	+	-	±	-
Xanthophyceae	+	-	-	-
Bacillariophyceae	+	-	+	-
Pyrrophyta	+	-	+	-
Cryptophyceae	+	-	+	-
Chloromonadophyceae	+(?)	?	?	?
Phaeophyta	+	-	+	-
Chlorophyta	+	+	-	-
Euglenophyta	+	+	-	-

note: “±” represents either high or low.

### ***Carotenoids***

It is well established that all photosynthetic organisms so far examined contain carotenoids in addition to chlorophylls and, following the work of Stanier and his colleagues (Griffiths *et al.*, 1955; Stanier and Cohen-Bazire, 1957), it would appear unlikely that any photosynthetic organism exists without carotenoids.

The carotenoids are a group of lipoidal pigments, ranging from yellow to red-orange in colour. Goodwin (1980) defines carotenoids as compounds basically consisting of eight isoprenoid units joined so that the arrangement of the units is reversed at the center of the molecule; thus the two central methyl groups are in a 1,6 position relative to each other while the remaining non-terminal methyl groups are in a 1,5 relationship. The carotenoid hydrocarbons are known as carotenes while the oxygenated carotenoids are known as xanthophylls. The series of double bonds in the resultant structure is known as the chromophore

and as a consequence of it, and the modifying influence of various additional structural features, the molecule is coloured and has the characteristic three peaked absorption spectrum of the carotenoids.

The carotenoids are reported to have a number of functions, of which perhaps the best documented is their contribution to photosynthesis as light-harvesting antennal pigments (ibid). In this role they show a wide range of efficiencies of energy transfer, with high and low efficiencies not showing any relationship with taxonomic groups (Goodwin 1980). Carotenoids are of interest not only for their functional role, but for their taxonomic significance as well. Their great variety and specificity, as well as their wide distribution in nature, makes them useful taxonomic markers (ibid).

### **Fossil Pigments**

It is well known that a variety of biological substances have been preserved in a relatively intact manner for periods of several hundred millions of years in extreme cases, e.g., proteinaceous compounds (Abelson, 1957), carbohydrates (summarized by Vallentyne, 1960), porphyrins (summarized by Dunning, 1960), and many other organic compounds.

### ***Chlorophyll derivatives***

One of the first studies of sedimentary chlorophyll degradation products (SCDP) was made by Trask and Wu (1930). Pigments arrive at the mud surface in fragments of organic detritus derived autochthonously from organisms living within the overlying water column. Included additionally is a vast collection of allochthonous material such as leaves from trees, shrubs, and shoreline plants. Smaller

amounts of pigments arrive in particles from soil humus layers and peat as they are eroded from the landscape (Gorham and Sanger, 1975; Sanger, 1988). Pigments that accompany all of the above are almost exclusively the insoluble and membrane bound type (Vallentyne, 1960). Water soluble pigments such as anthocyanins and phycobilins are usually destroyed prior to incorporation in sediments and have not been demonstrated to be useful in paleolimnology (Carpenter *et al.*, 1986; Sanger, 1988). During the past several decades, serious attempts have been made to fractionate and identify the algal pigments. Now we know that chlorophylls and their derivatives are universally present and abundant in freshwater and marine sediments (Orr and Grady, 1957; Cze Czuga and Czerpak, 1968; Koyama *et al.*, 1968; Tietjen, 1968; Sanger and Gorham, 1972; Whitehead *et al.*, 1973; Gray, 1974; Gorham and Sanger, 1975; Handa, 1975; Murray and Douglas, 1976; Brown *et al.*, 1977; Staub, 1977; Wetzel and Manny, 1978; Sanger and Crowl, 1979). All of the common forms and their chemical structures have been reported including chlorophyll a, b, c, d, bacteriochlorophyll and *Chlorobium* chlorophyll (Verenon, 1960; Brown, 1968). Chlorophyll a is present in all groups of photosynthetic organisms except some bacteria (Moss, 1968). It is the most abundant chlorophyll in living organisms and is also the most abundant form in sediments as pheophytin, pheophorbide a, chlorophyllide a, or in the isomerized or allomerized form (Daley *et al.*, 1977). Other chlorophylls occur similarly in derivative form. Undecomposed chlorophyll is less common and is usually reported from very recent sediments (Swain, 1985) or in poorly decomposed leaf fragments in cores, especially from meromictic lakes. The general picture emerging from the above studies, subject to future modification, is as follows.

- (a) Chlorophyll a, the most abundant green pigment in plants, is of relatively rare occurrence in sediments.
- (b) Chlorophyll b, which tends to lose its magnesium ion less readily than chlorophyll a, is found in at least some near-surface sediments.
- (c) With the exception of chlorophyll b and bacteriochlorophyll, all the sedimentary green pigments appear to be transformation products of known chlorophylls.
- (d) Two degradation pathways appear common; the first is more common than the second:

chlorophyll a --> pheophytin a --> pheophorbide a  
and

chlorophyll a --> chlorophyllide a --> pheophorbide a.

Removal of the central Mg atom from chlorophyll results in pheophytin; hydrolysis of the phytol moiety through the action of chlorophyllase produces chlorophyllide; these two reactions together result in pheophorbide formation (Daley *et al.*, 1977).

### ***Carotenoids***

The geologic occurrences of carotenoids differ from those of porphine derivatives. Carotenoids that occur in living organisms have also been isolated in pure form from freshwater and marine sediments. Carotenoids were first reported to occur in sediments by Trask and Wu (1930). Vallentyne (1956) in examining the epiphytic carotenoids isolated from sediments of a number of lakes, and tentatively identified myxoxanthin (echinenone) and postulated that its specificity to the blue-green algae would allow its use as a marker of these organisms. Echinenone has since been reported among the extraplastic carotenoids

produced in senescent Chlorophyta (Goodwin 1976), and it also occurs in zooplankton (Herring, 1968). These sources of the pigment are much less important than the blue-green algae (Goodwin, 1976), but make its use as a marker of the blue-greens less clear cut.

Zullig (1961) reported myxoxanthophyll in the sediments of Swiss lakes and noted its specificity in the blue-green algae. As these organisms are more common in eutrophic waters, it was postulated that this xanthophyll could be used as an indicator of lake primary productivity. Griffiths (1978) noted that Zullig's published spectra indicated oscillaxanthin rather than myxoxanthophyll.

Brown & Colman (1963) found the carotenoid oscillaxanthin in the sediments of McKay Lake near Ottawa. This xanthophyll is indicative of either *Oscillatoria agardhii* or *O. rubescens*, in temperate areas (Hertzberg and Liaaen, 1969). The specificity of this pigment to these *Oscillatoria* spp. is of interest because they are restricted to productive waters (Griffiths *et al.*, 1969).

### Sources of Sedimentary Pigments

Evidence indicates that most sedimentary organic matter is autochthonous. Only in oligotrophic lakes, where the total annual accumulations are sparse, does the receipt of allochthonous materials represent a substantial percentage contribution (Likens and Bormann, 1974; Gorham and Sanger, 1975; Cotter and Cowl, 1981). Detritus that arrives from allochthonous sources is often pigment-poor, having been exposed to frequent wetting and drying, oxidation, wide temperature variations, destruction by animals, bacteria, fungi and other agents which often reduces the pigment remains to near zero. Under these conditions, carotenoids are particularly vulnerable, decaying to colorless

derivatives and essentially disappearing as measurable entities. Only the most stable chlorophyll derivatives remain (Sanger, 1971a, b; Daley, 1973; Gray, 1974). The rate of pigment decay can greatly exceed the overall rate of organic matter decomposition, so receipt of terrestrial detritus largely serves to dilute the sedimentary pigments when concentrations are calculated per unit of sedimentary organic matter (Sanger, 1988).

The overwhelming contribution of sedimentary pigments seems to be from autochthonous sources. Major contributors are the plankton, floating pondweeds, periphyton, the rooted littoral macrophytes and, in some lakes, pigmented bacteria. Emergent shoreline plants are likely to be subject to the same destructive process as allochthonous detritus and are, therefore, less likely contributors to sedimentary pigments (Gorham and Sanger, 1975; Sanger and Crowl, 1979; Brown *et al.*, 1984).

When pure sedimentary chlorophyll (native chlorophyll) is found, it is likely to be derived from the aquatic macrophytes, since they are multicellular organisms, often with protective cellulose cell walls, whose chunks of undecomposed fragments can arrive unscathed at the mud surface. In a light-microscopic examination of mud samples from pondweed infested lakes (Sanger, 1988) indicated that numerous fragments of leaves, petioles, and stem tissue are present and may exhibit intact cell structure. Transmission electron microscopy of the same bits reveals intact chloroplast membranes and measurable amounts of undecomposed chlorophyll a and b (*ibid*).



## Pigment Sedimentation and Preservation

### *Sedimentation*

The interpretation of pigment stratigraphy in sediment columns depends on a clear understanding of the factors that influence the preservation of the molecules. The factors responsible for the degradation of carotenoids and chlorophylls are well known to organic chemists working on the isolation and identification of these pigments. Acidity, light, oxygen and high temperatures are all factors promoting the degradation of carotenoids and chlorophylls (Davies, 1976; Swain, 1985; Leavitt, 1988; Sanger, 1988). Once a pigment-producing organism dies, its pigment levels are no longer maintained and factors such as those noted above can reduce the remaining amount of pigment. Changing environmental conditions and possible differing rates of pigment degradation at the time of death and deposition of organisms may alter the amount of pigment preserved and thus complicate the interpretation of downcore pigment changes.

Once the organisms have died, the conditions experienced by the pigments still contained within the cell may change dramatically. Although some data exist for higher plants (Simpson *et al.*, 1976), no information is available for bacteria and algae. In senescent leaves, there is a decrease in total carotenoids with carotenes being more labile than xanthophylls (Simpson *et al.*, 1976). Xanthophylls' stability may be due to their esterification as they are liberated into the cytoplasm on disruption of the chloroplasts. The relative loss of carotenoids or their esterification may either proceed simultaneously or follow the decrease in chlorophyll, depending upon the species. There does not seem to be a direct relationship between chlorophyll and xanthophyll changes (Simpson *et al.*, 1976). It is difficult to say whether the conditions

within the dead bacterial cell would be similar to those described above because the bacteria thrive in a reducing environment (*ibid*).

Actual disruption of cell membranes also increases the likelihood of pigment degradation and this can come about by a number of mechanisms (Daley, 1973). Using a variety of algal species, Daley described the effects of bacterial lysing, grazing by zooplankton, and ingestion by phagotrophic algae. His study dealt only with algal chlorophyll breakdown products.

The effects of grazing on fucoxanthin, the characteristic carotenoid of diatoms and chrysophytes, has been investigated. This carotenoid, like the chlorophyll breakdown products, is first altered rather than being directly degraded to colourless products (Repeta and Gagosian, 1982). These authors showed that fucoxanthin is largely converted to a number of breakdown products while in the water column. The major product found in their sediment traps was fucoxanthinol. The authors have attributed this breakdown product to zooplankton and fish grazing since it can only be obtained by an enzymatic conversion under natural conditions. They also found a dramatic increase in this pigment in sediment traps (gathering fecal material) relative to suspended particulate matter samples (Repeta and Gagosian, 1982).

No study of the effects of grazing on the pigments of the photosynthetic bacteria has been carried out, but there are many reports indicating that photosynthetic bacteria are grazed (Sorokin, 1966; Culver and Brunskill, 1969; Takahashi and Ichimura, 1970; Gophen *et al.*, 1974; Caldwell and Tiedje, 1975; Sorokin and Donato, 1975; Gophen, 1977).

Factors such as the low rate of photo-oxidation in deep waters (Daley, 1973), slower decomposition rates in anoxic waters (Parkin and Brock, 1981), and high specific pigment content due to low light levels (Broche-Due *et al.*, 1978; Sistrom, 1978) all contribute to the preservation of large amounts of bacterial pigments in the sediments. The algae, on the other hand, being generally high in the water column, have a lower specific pigment content and are much more susceptible to degradation. Estimates of aerobic and anaerobic decomposition in meromictic Knaack Lake (U.S.A.) are also given by Parkin and Brock (1981). The rate of aerobic decomposition is estimated at  $188 \text{ g carbon m}^{-2} \text{ yr}^{-1}$  whereas the anaerobic rate is  $3.0 \text{ g carbon m}^{-2} \text{ yr}^{-1}$ . Thus the preservation of pigments under monimolimnetic anaerobic conditions is over 60 times better than for aerobic sediments (*ibid*).

### ***Preservation***

Once the pigments are deposited in the sediment, there is still the potential for further degradation. Under the right conditions, carotenoids may be preserved for long periods of time, which is exemplified in Searls Lake sediment (Vallentyne, 1960). Searls Lake sediments which were 20,000 years old still contained  $\beta$ -carotene. Vallentyne also noted that the xanthophylls disappeared more quickly than the carotenes. Belcher and Fogg (1964), however, found a decrease in carotenoids relative to organic matter in Esthwaite Water (U.K.). This lake is very eutrophic, and the authors concluded that carotenoids in the surface sediments were three times as concentrated as those in the deeper sediments.

Watts and Maxwell (1977) attempted to determine the rate of breakdown of carotenoids in the sediments of the Carico Trench, a 500 m deep structural depression in the continental shelf off Venezuela. In three sediment samples at 3 m of sediment (5,000 yr B. P.), 40 m (56,000 yr B. P.), and 170 m (340,000 yr B. P.) the total carotenoids were 28.5 ppm, 2.0 ppm, and 0.6 ppm respectively, giving them a greater rate of decrease than the total organic carbon. The authors suggested that these sediments underwent progressive reduction at rates dependent on the specific carotenoid content.

The rate of pigment degradation is difficult to determine because degradation processes and the influx rates of the various pigments vary independently, whereas in studies such as the ones referred to above, it was assumed that influx is constant with respect to organic matter, and that any changes observed are due to degradation.

Pigment degradation problems can be minimized by investigating sediments known to be conducive to good pigment preservation. Gorham and Sanger (1972) investigated the sediments of a meromictic lake both above and below the lake's chemocline. They found that the pigment preservation below the chemocline was much greater than above the chemocline. This they attributed to reduced biological degradation associated with the absence of oxygen. By investigating lakes in which the morphometry appears to ensure meromixis, or at least minimizes the overturn and thus oxygen entrainment, one probably minimizes degradation problems through most of the core.

Despite the problems involved in the interpretation of pigment stratigraphies, many useful insights have come out of such studies, as evidenced by those reviewed above. The choice of an appropriate site,

with good preservation of both sedimenting and deposited pigments, will circumvent many pigment degradation problems.

### **Interpretation of Pigment Stratigraphies**

Numerous studies in recent years have shed considerable light on the varied nature of lake evolution. Depending on the nature and climatic location of the basins, the general pattern that seems to be emerging is that at inception, northern lakes are generally high in nutrients but low in productivity because of their cold, turbid waters (Wetzel, 1983). Within a short period of several hundred years, lake production increases rapidly as vegetation and soil development stabilize erosion and reduce the cloudiness of the water (Gorham and Sanger, 1972; Manny *et al.*, 1978; Sanger and Crowl, 1979). This burst of productivity can occur in late glacial times, but more probably in the early post-glacial, depending on latitude. Southerly sites at the terminus of the ice edge experienced more rapid changes in vegetation after ice retreat in response to rapid climatic amelioration than did the more northerly areas (Davis, 1965; Wright, 1971; Sanger and Crowl, 1979; Cotter and Crowl, 1981). A lake's Productivity began to taper off throughout the mid-postglacial time and that pattern often continues into recent periods. Gradual oligotrophication is commonly interrupted by infilling of the basin with productive semi-aquatic marsh plants or by cultural eutrophication of the water (Hichman and Schweger, 1991).

Pollen data help to determine when the vegetation began to stabilize the substrata allowing soil development to begin and erosion of terrestrial materials to decrease. Cold, turbid water conditions gradually diminish and lake productivity begins to be governed more by nutrient loading rates and the depth of light penetration (Watson and Osborne,

1979). If the basin has a large littoral areas this could be a time of rapid colonization by aquatic macrophyte vegetation. Presence of the latter is governed by spectral composition and intensity of light that penetrates to the bottom of the lake (Jupp and Spence, 1977; Wetzel, 1983). Rapid pigment accumulation may result from the annual drift of littoral plant fragments to profundal sediments. Clues to the latter are found by examining the relative concentrations of pigments from planktonic organisms, especially blue-green algal pigments, compared to the more ubiquitous lutein and b-carotene. If the lake is largely dominated by phytoplankton, then there will be a predominance of carotenoids, especially the xanthophylls over chlorophyll derivatives (Gorham and Sanger, 1976). Extensive littoral areas could rapidly diminish as the outflow streams become entrenched and lake levels are lowered.

If a lake is located in a region that is high in carbonates, productivity may be diminished because the primary producers will compete with the carbonates for phosphorus, iron, and some of the other necessary micronutrients including manganese and reactive dissolved organics such as vitamin B<sub>12</sub> (Wetzel, 1970, 1972; Otsuki and Wetzel, 1972, 1974; White and Wetzel, 1975; Manny *et al.*, 1978). Phosphorus, which is often an important limiting factor to lake production, can co-precipitate with carbonates and can then be carried to the sediments where it remains unavailable to plants (Wetzel, 1983). These activities can cause a sustained lowering of phytoplankton productivity with resultant reduced concentrations of sedimentary pigments. White and Wetzel (1975) cite evidence that in high-carbonate sites a shift from phytoplankton domination to a high biomass of rooted macrophytes and their epiphytic microflora can occur because rooted

plants overcome the chemical nutrient limitations by uptake from the substrate. It is common in marl lakes to have carbonate concentrations inversely related to the concentration of sedimentary pigments and organic matter (Wetzel and Manny, 1978). As landscapes age, however, and erosion levels decline, the dissolved carbonates decrease and productivity and sedimentary pigments can rise as the sediment type shifts from marl or marly gyttja to gelatinous, pigment-rich, greenish gyttja (Sanger, 1988).

Rapid productivity changes have occurred in many lakes during recent times in response to cultural eutrophication that is documented by sudden increases of total pigments in the top meter of sediment. The cyanobacterial carotenoids, myxoxanthophyll and oscillaxanthin, increased dramatically in response to increased numbers of cyanobacteria that thrive on nutrients derived from burgeoning human settlements, forest clearance, and agricultural fertilization (Griffiths *et al.*, 1969; Griffiths and Edmondson, 1975; Griffiths, 1978; Zullig, 1982).

The sediments are the source of a careful record of pollution-related problems, including information that allows monitoring the succession of clean-up activities. These data are clearly of great value to human communities as they seek to lessen the undesirable effects of human activities on aquatic ecosystems (Rich, 1970; Adams *et al.*, 1978; Brugam, 1978; Davis and Norton, 1978; Guilizzoni *et al.*, 1981, 1982, 1983; Carney, 1982; Olson, 1982).

### Carbon Stable Isotopes

The ratio of carbon-12 to carbon-13 was used to determine the source of organic carbon in the sediments of Crawford lake. Elemental

carbon consists of a mixture of two stable isotopes,  $^{12}\text{C}$  and  $^{13}\text{C}$ , with relative abundances of about 98.894% and 1.106%, respectively (with a corresponding ratio  $^{12}\text{C}/^{13}\text{C} = 89.42$ ) (Winker *et al.*, 1982). It is well known that organic carbon in biological substances are markedly enriched in the light isotope ( $^{12}\text{C}$ ), while the heavy species ( $^{13}\text{C}$ ) is retained in the inorganic carbon such as carbonate ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbon dioxide ( $\text{CO}_2$ ) (Nier and Gulbransen, 1939; Murphey and Nier, 1941; Rankama, 1948; and Wickmann, 1952). Further studies indicate that the higher  $^{12}\text{C}/^{13}\text{C}$  ratios of biogenic substances result from both thermodynamic and kinetic isotope fractionations on the main assimilatory pathways (Craig, 1953; Park and Epstein, 1960). Craig (1954) proposed that several steps of carbon isotope fractionation exist in reactions of plant metabolism. The fractionation is also influenced by environmental conditions (Craig, 1954).

Differences in the isotopic composition of carbon-bearing substances are usually expressed in terms of the conventional  $\delta$ -notation giving the per mil deviation of the isotope ratio of sample (sa) relative to that of a standard (st), i.e. (Galimov, 1982):

$$\delta^{13}\text{C}_{\text{sa}} = \left[ \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sa}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{st}}} - 1 \right] \times 10^3 \quad \left( \text{‰}, \text{PDB} \right)$$

The standard commonly used is Peedee Belemnite (PDB) with  $^{12}\text{C}/^{13}\text{C} = 88.99$ , whose  $\delta^{13}\text{C}$ -value defines 0 ‰ on the  $\delta$ -scale. Positive values of  $\delta^{13}\text{C}$  would, accordingly, indicate an enrichment of heavy carbon ( $^{13}\text{C}$ ) in the sample relative to the standard while negative readings stand for its depletion, respectively.



### ***Carbon isotope fractionations and photosynthesis***

Biological (autotrophic) carbon fixation proceeds by a limited number of assimilatory pathways that transfer carbon dioxide ( $\text{CO}_2$ ), bicarbonate ion ( $\text{HCO}_3^-$ ) and carbon monoxide ( $\text{CO}$ ) from the inorganic carbon reservoir to the biosphere (Schidowski *et al.*, 1983). The inorganic carbon compounds are primarily fixed as  $\text{C}_3$  compounds (phosphoglycerate, pyruvate, phosphoenolpyruvate),  $\text{C}_4$  compounds (Oxaloacetate) and  $\text{C}_2$  compounds (acetate, acetyl coenzyme-A). Biological carbon fixation is fixation of  $\text{CO}_2$  by green plants and photoautotrophic protists (e.g. algae) and prokaryotes (photosynthetic bacteria including cyanobacteria) (*ibid.*).

All pathways of autotrophic carbon fixation lead to a preferential incorporation of isotopically light carbon into cell material. The biochemistry of carbon isotope fractionations during  $\text{CO}_2$  uptake and metabolism has been examined in numerous investigations (Park and Epstein, 1960; Wong and Sackett, 1978; Wong, Sackett and Benedict, 1975; Wong, Benedict and Kohel, 1979; Sirevag *et al.*, 1977; Estep *et al.*, 1978; O'Leary, 1982; Winkler *et al.*, 1982).

In a particular growth environment,  $\text{C}_3$  plants are enriched in  $^{12}\text{C}$  by 12-14 ‰ over  $\text{C}_4$  plants (Tregunna *et al.*, 1970; Smith and Brown, 1973). Investigations (Bender, 1971; Craig, 1953; Deevey and Stuiver, 1964; Lowdon and Dyck, 1974; Oana and Deevey, 1960; Wickman, 1952) indicate that isotopic composition of algae is intermediate between those of  $\text{C}_3$  and  $\text{C}_4$ -type plants, but tends more towards a slight  $^{13}\text{C}$  enrichment.

### ***Carbon isotope fractionation***

The  $^{13}\text{C}$  content of carbon fixed photosynthetically by an aquatic plant may depend on environmental factors such as temperature, light level, pH of the water, the availability of carbon and oxygen of the water (Deuser *et al.*, 1968; Calder and Parker, 1973).

In an aqueous environment the carbon isotope fractionation may depend on chemical species of carbon ( $\text{CO}_2$  and  $\text{HCO}_3^-$ ) existing in the water and which of these is used by the plant (Calder and Parker, 1973). As the relative distribution of  $\text{CO}_2$  and  $\text{HCO}_3^-$  varies with pH, so too the carbon isotope fractionation in an aqueous environment may be pH dependent (*ibid*).

Calder and Parker (1973) did not observe a significant difference in  $\delta^{13}\text{C}$  for the blue-green algae grown at 30 and 39 °C. However, Deuser *et al.* (1968) found that the fractionation between  $\text{HCO}_3^-$  and plankton was -25 to -27 ‰ and decreased systematically by 0.35 ‰ per degree Celsius temperature rise.

The algal carbon isotope fractionation on carbon supply was investigated by Abelson and Hoering (1961). The photosynthetic fractionation of carbon by blue-green algae was studied by Calder and Parker (1973) and found to depend on the  $\text{CO}_2$  concentration.

### ***The $^{137}\text{Cs}$ dating method***

A large amount of  $^{137}\text{Cs}$  was produced in nuclear weapon tests and deposited on the earth as fallout (Health and safety Laboratory, 1977). Cesium entering the terrestrial aqueous system has been found to sorb strongly onto clay particles. The bonding of cesium to minerals permits the use of this radionuclide to trace sediment particles in a

wide variety of systems. Two time periods can be discerned from the measurements of  $^{137}\text{Cs}$  in recent core sections (Pennington *et al.*, 1973; Ashley and Moritz, 1979): (a) the depth where the 1963 peak is found, and (b) the depth where the  $^{137}\text{Cs}$  is first detected, circa 1954.

### ***The $^{210}\text{Pb}$ dating method***

The use of decay products of naturally occurring  $^{226}\text{Ra}$  for sediment geochronology was first outlined by Goldberg (1963). The decay chain of  $^{226}\text{Ra}$  proceeds through several radionuclides with short half-lives to the long-lived  $^{210}\text{Pb}$ . The basic principle of  $^{210}\text{Pb}$  dating is that radon gas,  $^{222}\text{Rn}$ , is emitted to the atmosphere from the lithosphere, surface waters, and airborne dust, and this gas decays to form  $^{210}\text{Pb}$ . This change in phase isolates radon from its radium precursor and destroys the initial secular equilibrium (Appleby and Oldfield, 1983). A new secular equilibrium is then reached by the radon with the longest-lived product  $^{210}\text{Pb}$ .  $^{210}\text{Pb}$  and other  $^{222}\text{Rn}$  daughter products rapidly become attached to atmospheric aerosols and are removed by dry fallout and precipitation (Nevissi and Schell, 1980). This continuous source of  $^{210}\text{Pb}$  provides a widespread flux to land and water surfaces.

Organic-rich soil horizons are efficient in retaining  $^{210}\text{Pb}$  from atmospheric precipitation which can then be transported to rivers mainly by soil erosion (Robbins, 1978). After entering the river systems, the  $^{210}\text{Pb}$  is adsorbed on suspended particles and removed rapidly from the water column (Goldberg, 1963). Most of the  $^{210}\text{Pb}$  entering lakes comes directly from atmospheric input across the atmosphere-water interface and is deposited in the bottom with the sedimentation of the suspended particulate matter.

By measuring the  $^{210}\text{Pb}$  concentrations in several different sediment horizons, the rates of sediment accumulation can be calculated. However, because  $^{210}\text{Pb}$  is also formed *in situ* from the terrigenous  $^{226}\text{Ra}$  present in the sediment, this “supported” amount must be subtracted from the total concentration to obtain the unsupported  $^{210}\text{Pb}$ . The unsupported  $^{210}\text{Pb}$  represents the amount added to the water column from atmospheric sources.

The change in concentration of  $^{210}\text{Pb}$  by decay with time,  $t$ , varies as:

$$-dN/dt = \lambda N \quad (1)$$

where  $N$  = disintegration rate of  $^{210}\text{Pb}$ , and  $\lambda$  = decay constant ( $0.03114 \text{ yr}^{-1}$ ).

By making the assumption that the  $^{210}\text{Pb}$  once deposited with the sediment remains firmly fixed, the time of deposition can be determined from the decay. The age at any depth,  $z$ , is found by integrating equation (1):

$$t = 1/\lambda \ln(N_0/N) \quad (2)$$

The sedimentation rate is found from (2) by replacing  $t$  with the quotient  $z/s$  and rearranging:

$$s = \frac{z\lambda}{\ln(N_0/N)} \quad (3)$$

The average rate of input of  $^{210}\text{Pb}$ ,  $r$ , at any particular sampling location in a lake can be determined by integrating over its lifetime:

$$r = (N/A)\lambda \text{ dpm g}^{-1} \text{ cm}^{-2} \text{ yr}^{-1} \text{ (Appleby and Oldfield, 1983)} \quad (4)$$

in which  $N$  ( $\text{dpm g}^{-1}$ ) is the total unsupported  $^{210}\text{Pb}$ ;  $A$  ( $\text{cm}^2$ ) in a given area of weighed sections.

Profiles of unsupported  $^{210}\text{Pb}$  activities in sediment cores may be used to establish sedimentary geochronologies by several different numerical models. Because the dates are very model sensitive, it is necessary to consider carefully the applicability of each model to the experimental observations. There are two basic models to be considered: the constant initial concentration (CIC) model and the constant rate of supply (CRS) model. Both models assume that there is a constant input of unsupported  $^{210}\text{Pb}$  to the lake and a constant residence time of  $^{210}\text{Pb}$  in the lake water column. Additionally, both models assume that there is no migration of the  $^{210}\text{Pb}$  within the sediment or loss from the sediment to the overlying water. The CIC model makes the assumption that in each stage of sediment accumulation the initial concentration of unsupported  $^{210}\text{Pb}$  was constant, regardless of any change in the rate of bulk sediment accumulation. The resulting corollary is that the unsupported  $^{210}\text{Pb}$  profile must decrease monotonically with depth (time) in an undisturbed core. This implies that either the sedimentation rate remains constant or the rate of bulk sediment accumulation changes and that the unsupported  $^{210}\text{Pb}$  concentration changes in the same manner. The CRS model assumes that the flux of unsupported  $^{210}\text{Pb}$  is constant over the whole period considered (Appleby and Oldfield, 1983).

## Methods

### 1. Sampling:

#### a) Crawford Lake Monimolimnion Cores:

- Two cores were taken from Crawford Lake on April 8, 1992 at a water depth of 21 m using a Kajak Gravity Corer. The length of the sampler tube is about 90 cm and the diameter of the tube is 7.5 cm. The results of the analysis from the first Crawford Lake core were not used as this was a practice core.
- The overlying water above the sediment in the core tube was siphoned off by putting a "U" - shaped tube just above the surface of the sediment. This was done very carefully so that the sediment was not disturbed.
- In order to avoid undue sediment mixing, the core sample was brought to the shore in such a way as to minimize its mixing.
- The core was sectioned at 2 mm intervals from 0 to 1 cm and at 5 mm intervals from 1 cm to 20 cm. Below a depth of 20 cm, the core was sectioned at 1 cm intervals. A piston rod was used to extrude the sediments from this 50 cm long core. A 2 mm, 5 mm or 1 cm thick ring was placed on the top of the core tube to estimate how much sediment was extruded at each depth in the core.

#### b) Crawford Lake mixolimnion Cores:

One Kajak sediment core was removed from 8.2 m. The overlying water was removed by a siphon as previously noted. The core sediment was then extruded and cut. The sliced sediments (0-1 cm, 1-2 cm, 2-3 cm, and 1 cm of the bottom layer) were kept in plastic bags and stored in a refrigerator after they were brought back the laboratory.

**c) Lady Evelyn Reservoir Hypolimnion Core:**

One Kajak sediment core was removed from the Snake Point (30 m of water depth) in Lady Evelyn Reservoir (Fig. 3). The overlying water was removed by a siphon. The 25 cm long core was cut into 1 cm thick sections. The sliced sediments were kept in plastic bags and stored in a refrigerator after they were brought back to the laboratory.

**2. Extracting the pigment samples:**

- About 20 ml of a 90% acetone solution was added to each of the wet samples and centrifuged at 5,000 rpm.
- Four consecutive 20 ml volumes of 90% acetone were combined and then brought up to 100 ml with the same acetone solution.

Note: The above procedures were conducted under dim light and low temperature (about 4 °C) to prevent pigment decomposition.

**3. Preparing solutions for pigment analysis:**

**a) Chlorophyll derivatives (CD):**

10 ml of the extract were removed for CD measurement (Sanger and Gorham, 1972).

**b) Myxoxanthophyll and oscillaxanthin:**

- 50 ml of the acetone extract was transferred to a 125 ml separatory funnel and 30 ml petroleum ether was added with a volumetric cylinder.
- The hypophase was collected in an evaporating dish and the epiphase discarded.
- The evaporating dishes were placed in an air jet to dry the solution.

- After drying, 5 ml of ethanol was added to the dish containing the hypophasic pigments.
- After the dried pigments were redissolved in ethanol, the solution was poured into a standard screw cap test tube, capped and kept in the refrigerator (Swain, 1985).

**c) Total carotenoids (TC):**

- 200 g KOH was dissolved in 1,000 ml methanol to make a 20% KOH-methanol (weight/volume) solution.
- 20 ml acetone solution was transferred using volumetric pipettes to a 125 ml separatory funnel and added to 10 ml of 20% KOH/methanol.
- This mixture was refrigerated for 2 hrs.
- The carotenoids were extracted using 30 ml of petroleum ether in a standard separatory funnel. The hypophase was discarded and the epiphase preserved.
- The petroleum ether extract was washed five times using distilled water.
- The neutral extracts were poured into tubes with screw caps and placed into the refrigerator as described by Sanger and Gorham (1972).

**4. Pigment Analysis**

- Chlorophyll derivatives (CD) were measured at 665 nm with one portion of the extract and expressed as absorbance per gram organic matter dissolved in 100 ml of solvent, a standard unit for paleolimnological work (Sanger and Gorham, 1972).



- Native chlorophyll was expressed as the proportion of chlorophyll not degraded to phaeopigments, as measured by the acidification with 0.003 M HCl and calculated using the equation of Lorenzen (1967):

$$\text{per cent native chlorophyll} = \frac{665B-665A}{0.7(665A)} \times 100$$

where 665B is the absorbance at 665 nm before acidification and 665A is the absorbance at 665 nm after acidification.

- Total carotenoids (TC) were measured by first saponifying the acetone aliquot and then the carotenoids were extracted with petroleum ether. TC were determined by measuring absorbance at 448 nm (Sanger & Gorham, 1972), and expressing the results in the same units as for chlorophyll derivatives.
- Oscillaxanthin and myxoxanthophyll were determined using the last portion of the acetone extract by first adding petroleum ether to remove TC and CD. Then the acetone-water hypophase was dried under an air jet and dissolved again in ethanol. The concentration of the two blue-green algal pigments was determined by a trichromatic method using the following absorbance wavelengths: 412 nm, 504 nm, 529 nm.

The concentration of each pigment in the sediment was calculated as:

$$\text{g pigment /g organic matter} = \frac{10,000 (V)(A)}{(E)(P)(g \text{ org.})}$$

where (A) is the appropriate major peak absorbance from equation:

$$O_{495} = 1.27(1.266A_{529} - 0.219A_{504} - 0.081A_{412})$$

$$M_{473} = 1.20(1.358A_{504} - 1.308A_{529} - 0.031A_{412})$$

(g org.) is the weight of organic matter in the extracted sediment, (P) is the proportion of the pigment extract used in this measurement, (V) is the volume of ethanol extract in ml and (E) is the appropriate extinction coefficient (1450 for oscillaxanthin and 2100 for myxoxanthophyll; (Griffiths, 1978).

## 5. Algal composition:

In addition, pigment analysis samples of the surface layers of the three cores were made for microscopic analysis using a Nikon microscope equipped with a photoautomatic unit for colour film exposures.

The algal composition of surface sediments was characterized using Prescott (1970) and Smith (1950) for algal identification.

## 6. SCUBA Diver analysis

The chemocline sediments (8.2-10.6 m) were photographed by Mr. David Gilchrist using an underwater camera and lights. Mr. Gilchrist was accompanied in 1989 by Mr. Jim Lockhart. In 1993, Mr. Gilchrist also collected sediment cores which Dr. Dickman and I examined using the Nikon microscope.

## 7. Water content:

- About 10 g wet weight of sediment was placed into a small beaker, weighed, and then placed in a drying oven.
- The beakers were heated for 4 h at 105 °C.

- After drying and cooling, the beakers with the sediments in them were weighed again.

### **8. Organic and carbonate carbon content:**

Determination of organic and inorganic carbon in the sediment samples was carried out by the method of "loss on ignition". The ignition loss procedure described below was a modification of the procedure described by Dean (Dean, 1974):

- About 1 g powdered sample was dried in an oven for one hour at 110 °C using a preweighed ceramic crucible. After cooling to room temperature, the sample and crucible were weighed. This gave the dry weight of the sample which was the basis for all weight loss calculations.
- The sample and crucible were then placed in a muffle furnace and heated to 550 °C for four hours. After cooling to room temperature, the sample was again weighed. The difference between this weight and the dry weight was the amount of organic carbon loss on ignition (LOI).
- The sample was returned to the muffle furnace and heated to 950 °C for four hours. The weight loss between 550 to 950 °C was the amount of CO<sub>2</sub> evolved from the carbonate in the samples.

### **9. Lead-210 and Cesium-137 analysis**

#### **a) <sup>210</sup>Pb dating method:**

<sup>210</sup>Pb activity was determined through the extraction and counting of a daughter isotope, <sup>210</sup>Po. Extraction of <sup>210</sup>Po will be done with methods developed by Flynn (1968) and modified by Han (1986). The <sup>210</sup>Po and a <sup>208</sup>Po internal trace was plated onto silver planchets and

counted by Ortec surface barrier detector in a vacuum chamber and recorded by a 4096-channel multichannel analyzer (Han et al., 1986). Supported  $^{210}\text{Po}$  was calculated from  $^{226}\text{Ra}$  measured by a Ortec gamma spectrometer (by Mr. Liang Xiang in Nanjing Institute of Geography and Limnology, Academia Sinica). The sediment age was calculated using the Constant Rate of Supply (c.r.s.) model (Appleby & Oldfield, 1978) according to the pattern of  $^{210}\text{Pb}$  activity-depth curve (Han 1992; Xiang and Han, 1992) and compared with the age from  $^{137}\text{Cs}$  dating.

**b)  $^{137}\text{Cs}$  dating method:**

$^{137}\text{Cs}$  activity will be determined by a Ortec gamma spectrometer with dried sediment sample of 10 g (by Mr. Liang Xiang in Nanjing Institute of Geography and Limnology, Academia Sinica). A maximum concentration was found at one depth and the date of 1963 placed on this level, based on the historical pattern of atmospheric fallout (Health and Safety Laboratory, 1977).

**c) Pigment accumulation rate calculations:**

The accumulation rate of pigments was calculated first by multiplying the sedimentation rate (presented as sedimentation flux with a unit of  $\text{g cm}^{-2} \text{yr}^{-1}$ ) with organic matter content and then by multiplying the result by the concentration of the pigment. The accumulation rate of the pigment is the result of this calculation (Han, 1986).

**10. The stable isotopes of organic carbon in the sediments**

The element carbon consist of a mixture of two stable isotopes,  $^{12}\text{C}$  and  $^{13}\text{C}$ , whose relative abundances in geochemically undifferentiated

carbonaceous material come close to 98.894% and 1.106%, respectively (Wong and Sackett, 1978).

Differences in the isotopic composition of carbon-bearing substances are usually expressed in terms of the conventional  $\delta$ -notation giving the permil deviation of the isotope ratio of sample (sa) relative to that of a standard (st), i.e.(ibid):

$$\delta^{13}\text{C}_{\text{sa}} = \left[ \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sa}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{st}}} - 1 \right] \times 10^3 \quad \left( \text{‰}, \text{ PDB} \right)$$

The standard commonly used is Peedee Belemnite (PDB) with  $^{12}\text{C}/^{13}\text{C} = 88.99$ , whose  $\delta^{13}\text{C}$ -value defines 0 ‰ on the  $\delta$ -scale. Positive value of  $\delta^{13}\text{C}$  would, accordingly, indicate an enrichment of heavy carbon ( $^{13}\text{C}$ ) in the sample relative to the standard while negative readings stand for its depletion.

The  $\delta^{13}\text{C}$  of organic matter in the sediments was measured with a sealed tube oxidation-combustion procedure (Stump and Frazer, 1973). with a Matthew-251 Mass Spectrometer (by Dr. Lei Ji and Mr. Liang Xiang in Nanjing Institute of Geography and Limnology, Academia Sinica).

## Results

### 1. Description of the cores:

#### *Crawford Lake Monimolimnion Core*

The Crawford Lake sediment core was collected on April 8, 1992. The core was divided into five units (Fig. 4) based on its sediment characteristics, i. e. colour, percent organic matter, lead-210 estimated sedimentation rate, pigment concentrations and the chronology related to the history of the land use of the surrounding areas of Crawford Lake inferred by the pollen in the sediments of the lake (Boyko, 1978) and lead-210 dating of the core. Pine needles were found at several depths (16-21 cm, 21-33 cm, 36-37 cm, 38-40 cm, 41-42 cm, and 46-47 cm). The needles probably represent elevated pine tree densities and/or release of needles following the selective cutting of the pine trees in the Crawford Lake watershed near the lake. In the late 1800's a saw mill was operated in the Crawford Lake watershed (Boyko, 1978).

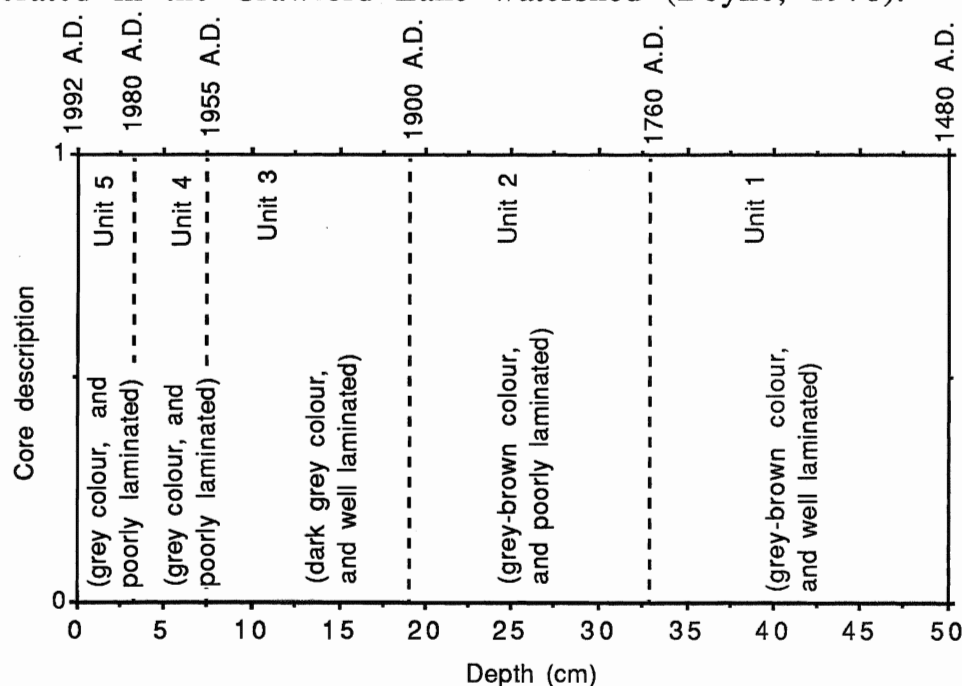


Fig. 4. Characteristics of the core from Crawford Lake (April 8, 1992).

### *Lady Evelyn Reservoir core comparison*

A second lake was cored in order to compare Crawford Lake pigment composition with a lake where the sediment pigment preservation conditions were less than ideal.

The Lady Evelyn Reservoir sediment core was taken on 28 July, 1992 in 30 m of water near Snake Point on Lady Evelyn Reservoir (Fig. 3) on July 28, 1992. Three stratigraphic units characterized the core (Fig. 5). The uppermost unit was deposited after a cement dam was constructed in 1972, the middle unit was deposited after the initial damming of the lake in 1916-1924 and the third (deepest) unit was deposited prior to reservoir construction (Fig. 5).

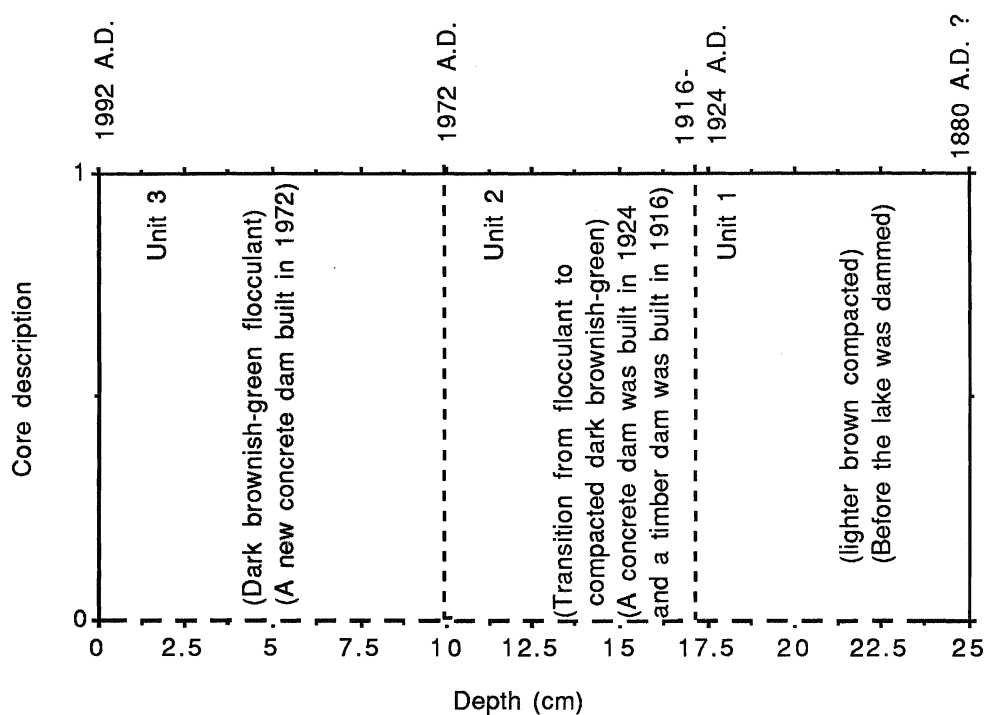


Fig. 5. Characteristic of the core from Lady Evelyn Reservoir.

### *Crawford Lake Mixolimnion Core*

Characteristics of the mixolimnion-mud water interface core collected on May 22, 1993 are described in Table 2.

One sample of the algal mat was collected in a plastic bag by Mr. Gilchrist on 22 May, 1993. The algal mat had streaks of white fungus running on the top of the algal layer (Dickman, pers. comm.). The algal mat layer extended to a maximum depth of 14.2 m. At

Table 2. Description of the Crawford Lake chemocline core

Core number	Characteristic	Sliced
Core 1	This core was collected at water depth of 8.2 m with white fungus covered the red-brown alga	0-1 cm 1-2 cm 2-3 cm 9-10 cm

a depth of 14 m the red-brown coloured algal layer (Fig. 6A) was thicker than it was at 12 m and gas bubbles appeared to be formed under the mat pushing it up in places (Fig. 6B). A fine silt was

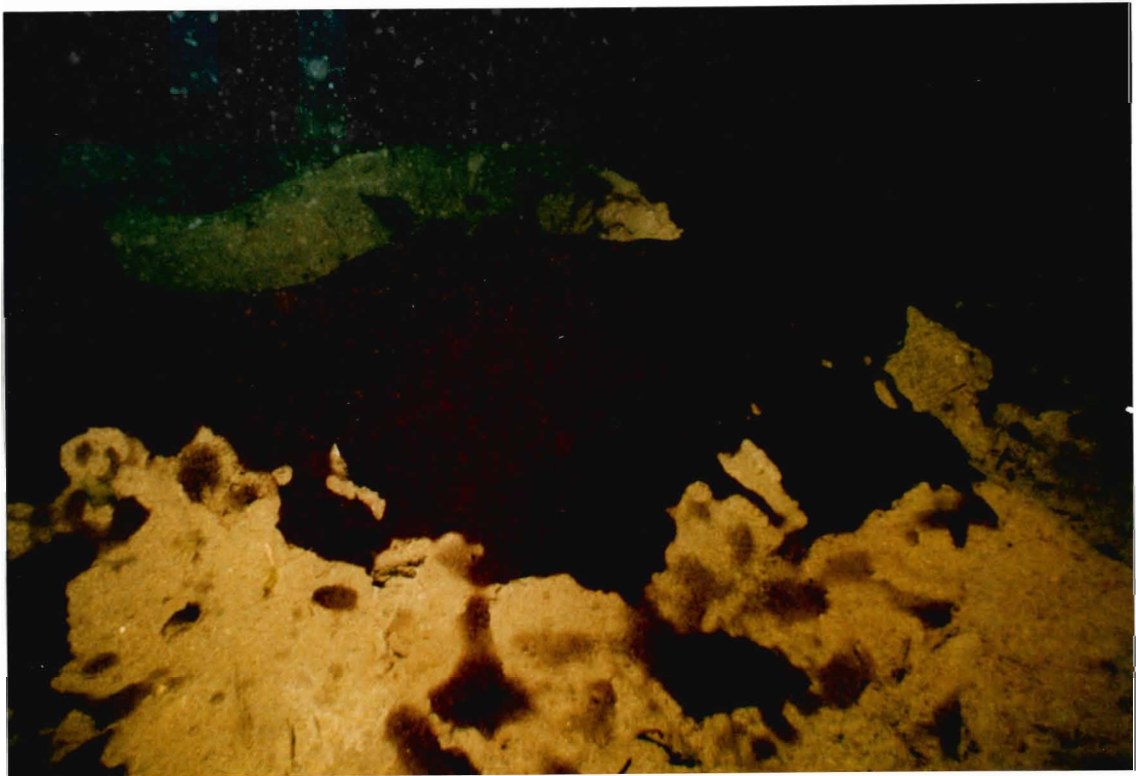


Fig. 6A. An underwater (12-14 m) photograph of cyanobacterial "mat" surrounded in part, by a white marl where the lake sediments are uncolonized by the algal mat.



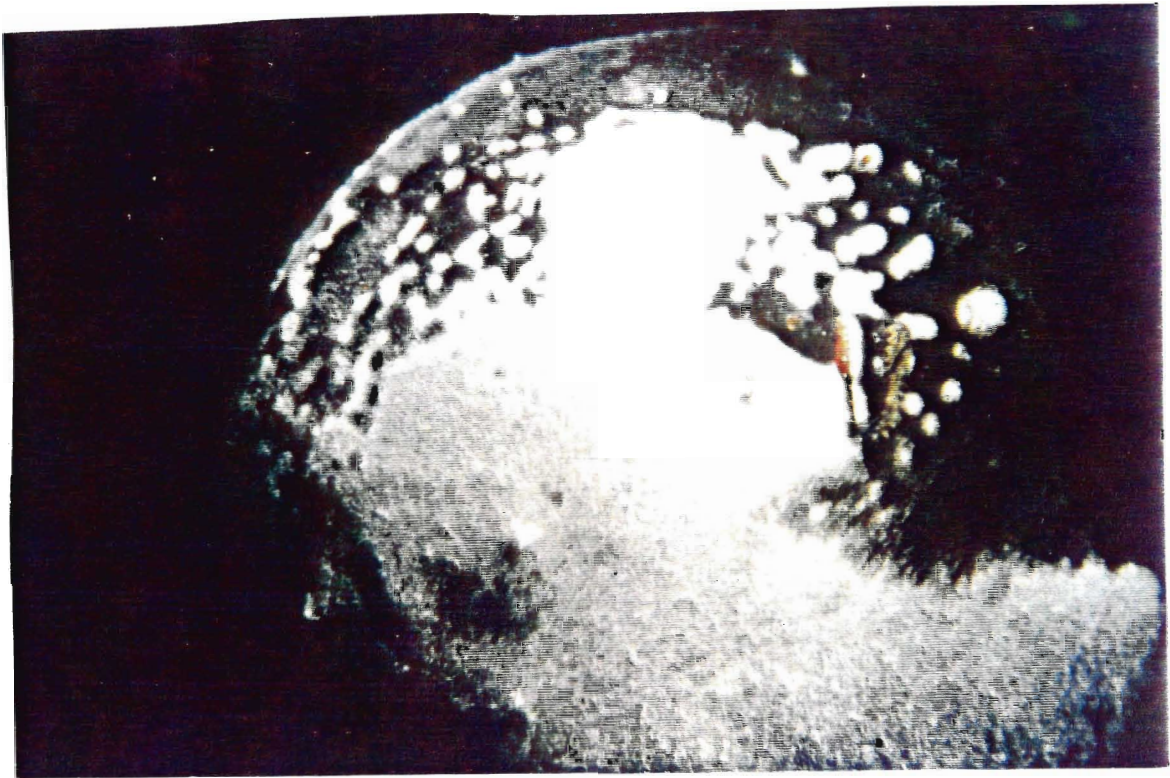


Fig. 6B. Gas bubble beneath the "algal mat" layer in Crawford Lake.

Photo by D. Gilchrist September, 1989 at 13 m on the bottom of Crawford Lake. The white material is a fungus growing on the algal mat. The bubble was approximately 7 cm in diameter.

deposited in a few places on the mat but the white fungus covered about 40-50 % of the mat. The maximum mat thickness was about 4 mm in thickness at a depth of 12 m.

#### *Microscopic Analysis of the Crawford Lake Cores*

At a depth of 8 to 14 m the bottom of Crawford Lake is covered with a 2-4 mm thick cyanobacterial mat. The mat is composed of an epipelagic algal layer and appears to be made up of 2 sublayers (Dickman, pers. comm.). The uppermost layer is only about 2 mm thick and

consists of a yellow green gelatinous material made up of the secretions of millions of blue green algae belonging to the family *Oscillatoriaceae*. The dominant members of this layer are *Oscillatoria* spp., *Lyngbya* spp. and *Spirulina princeps* (Fig. 7).

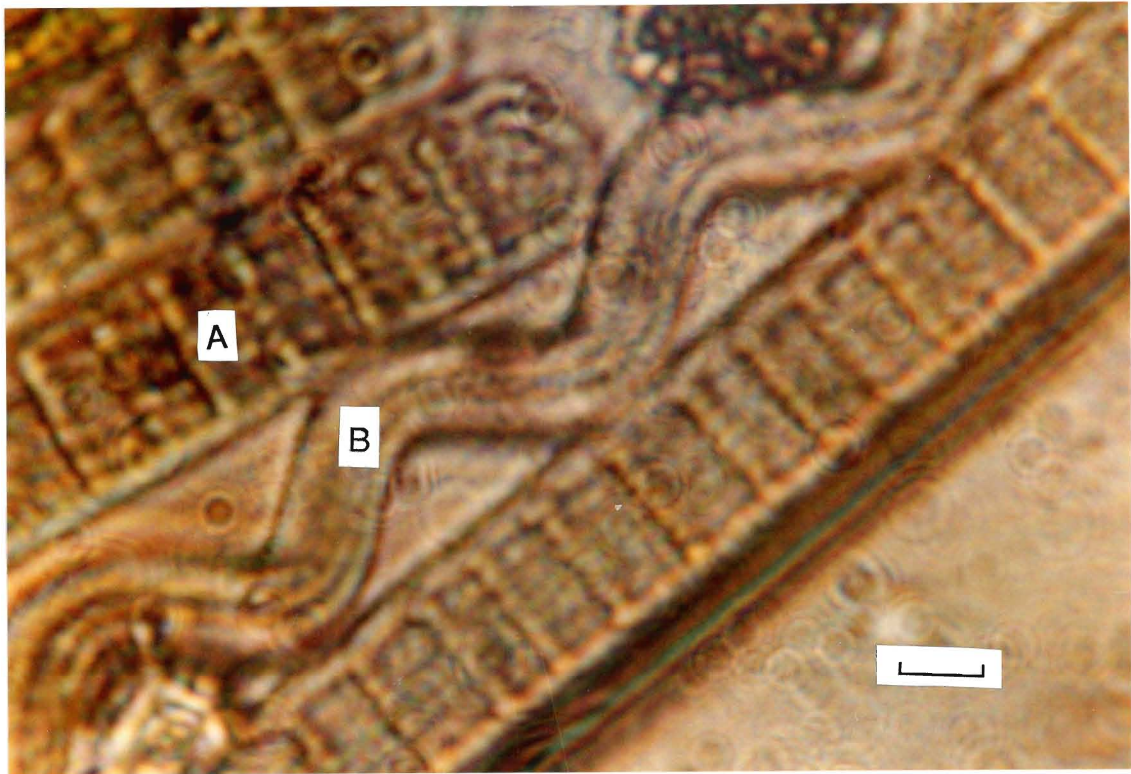


Fig. 7. *Oscillatoria* sp. (A), and *Spirulina princeps* (B). The horizontal line represents a distance of 2  $\mu\text{m}$ .

Below this layer is a 1-2 mm thick dense gelatinous layer which is a dark greenish-brown colour. This layer is composed of the mucillagenous and proteinaceous sheaths of millions of *Lyngbya* filaments (trichomes).

Below these layers is a non-gelatinous yellow green coloured sediment composed primarily of diatoms and unicellular algae and

bacteria which appear to have settled out of the overlying water column (Dickman and Han in prep.).

It is possible that the motile blue green algae which dominate layers one and two are able to avoid being literally buried by the continuous "rain" of sedimenting dead and dying phytoplankton and detritus by continually moving up on top of the settled particles. Were this not the case, the cyanobacterial "mat" would soon be covered in detritus and would disappear from view. Because the mat members are motile and photosynthetic, photosynthesis would be limited or curtailed by reduction of light availability as more and more detritus piled up on top of the mat were mat members non-motile (Dickman and Han in prep.).

Competition for light between phototrophic bacteria and phytoplankton in Crawford Lake was described by Rybak and Dickman (1988) but the possibility that hypophasic carotenoids from cyanobacteria were also important was never mentioned because the algal mat was not discovered until 1988.

## **2. Sedimentation rate**

### ***Sedimentation rate estimated by $^{210}\text{Pb}$ dating method***

The sedimentation rates deduced using  $^{210}\text{Pb}$  based on the  $^{210}\text{Pb}$  CRS model (Appleby and Oldfield, 1978) ranged from 1.65 mm yr<sup>-1</sup> to 2.80 mm yr<sup>-1</sup> at 0-5 cm with an average value of 2.21 mm yr<sup>-1</sup>. At a depth of 5.0-7.0 cm the sedimentation rate decreased from 2.80 to 1.65 mm yr<sup>-1</sup> (Table 3).

Table 3. Activities of  $^{210}\text{Pb}$  in the sediments of Crawford Lake, ages in years and sedimentation rates based on the  $^{210}\text{Pb}$  CRS model (Appleby and Oldfield, 1978)

Actual depth (cm)	Mass depth (g cm <sup>-2</sup> )	Total $^{210}\text{Pb}$ (dpm g <sup>-1</sup> )	CRS model ages (year)	CRS model rate (mg cm <sup>-2</sup> yr <sup>-1</sup> ) (mm yr <sup>-1</sup> )	
0.0-0.5	0.018	64.69	1.48	11.9	1.65
0.5-1.0	0.051	58.37	4.25	12.1	2.02
1.0-1.5	0.082	49.23	6.73	13.3	2.02
1.5-2.0	0.114	39.03	8.90	15.8	2.72
2.0-2.5	0.143	43.25	10.98	13.3	2.14
2.5-3.0	0.174	40.32	13.27	13.3	2.22
3.0-3.5	0.201	39.23	15.30	12.9	2.80
3.5-4.0	0.227	44.78	17.60	10.5	1.75
4.0-4.5	0.253	39.43	20.00	11.1	2.64
4.5-5.0	0.277	36.58	22.15	11.2	2.07
5.0-5.5	0.306	36.96	24.93	10.1	1.58
5.5-6.0	0.335	38.33	27.97	8.9	1.71
6.0-6.5	0.361	36.67	30.97	8.5	1.64
6.5-7.0	0.387	32.57	34.00	8.7	1.67
7.0-7.5	0.413	24.53	36.71	10.8	2.08
7.5-8.0	0.440	27.23	39.49	8.8	1.57
8.0-8.5	0.466	16.43	41.96	13.9	2.90
8.5-9.0	0.494	24.99	44.78	8.2	1.24
9.0-9.5	0.526	17.70	48.20	10.6	1.83
9.5-10.0	0.556	13.95	50.84	12.6	1.97
10.0-10.5	0.587	12.26	53.22	13.5	2.25
10.5-11.5	0.646	9.87	57.17	15.1	1.70
11.5-12.5	0.726	9.47	62.82	13.3	1.87
12.5-13.5	0.796	9.55	68.56	11.0	1.62
13.5-14.5	0.860	9.37	74.89	9.2	1.53
14.5-15.5	0.915	8.46	81.11	8.6	1.72
15.5-16.5	0.969	7.07	87.41	8.7	1.48
16.5-17.5	1.023	6.08	93.73	8.5	1.77
17.5-18.5	1.071	6.85	100.46	6.0	1.25

The sedimentation rate increased between 9.0-12.5 cm ( $1.62\text{--}2.25\text{ mm yr}^{-1}$ ) and decreased between 12.5-18.5 cm ( $1.25\text{--}1.77\text{ mm yr}^{-1}$ ) (Fig. 8).

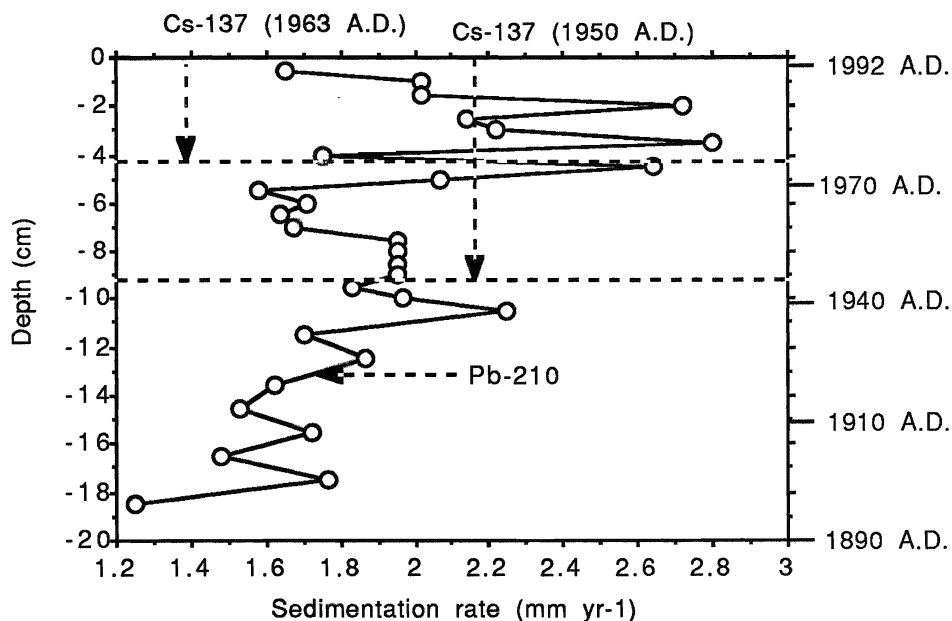


Fig. 8. The sedimentation rates of the Crawford Lake core based on  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  analyses

#### *Sedimentation rate as estimated by $^{137}\text{Cs}$ dating method*

$^{137}\text{Cs}$  data are given for the core of Crawford Lake in Table 4. Maximum  $^{137}\text{Cs}$  activities occurred at 3.5-4.0 cm which corresponds to 1963 (Stiller and Assaf, 1973; McHenry *et al.*, 1980).  $^{137}\text{Cs}$  was detected at 9.0 cm which corresponds to 1950. In my discussion section I compare Cs-137 and Pb-210 estimates of age at 9 cm. An average sedimentation rate in the Crawford Lake core was calculated as  $1.38\text{ mm yr}^{-1}$  above 4 cm and  $2.14\text{ mm yr}^{-1}$  above 9.0 cm by the  $^{137}\text{Cs}$  method (Table 3; Fig. 8).

Table 4.  $^{137}\text{Cs}$  Activity in the sediments from Crawford Lake

Actual depth (cm)	Mass depth (g cm <sup>-2</sup> )	$^{137}\text{Cs}$ (Bq kg <sup>-1</sup> )	Sedimentation rate (mm yr <sup>-1</sup> ) and
0.0-0.5	0.018	40.48	comment  1.38 mm yr <sup>-1</sup> At 4 cm (circa 1963) $^{137}\text{Cs}$ peaked at 234 Bq kg <sup>-1</sup>
0.5-1.0	0.051	58.03	
1.0-1.5	0.082	57.09	
1.5-2.0	0.114	43.32	
2.0-2.5	0.143	68.86	
2.5-3.0	0.174	80.93	
3.0-3.5	0.201	214.79	
3.5-4.0	0.227	233.52	
4.0-4.5	0.253	178.84	2.14 mm yr <sup>-1</sup> $^{137}\text{Cs}$ was undetectable before 1950
4.5-5.0	0.277	164.60	
5.0-5.5	0.306	112.71	
5.5-6.0	0.335	91.04	
6.0-6.5	0.361	55.32	
6.5-7.0	0.387	32.93	
7.0-7.5	0.413	22.68	
7.5-8.0	0.440	17.91	
8.0-8.5	0.466	19.16	
8.5-9.0	0.494	10.75	

### 3. Pigment stratigraphy

#### *Organic matter in Crawford Lake and Lady Evelyn Reservoir*

With few exceptions, Crawford Lake organic matter, as indicated by loss on ignition (LOI) (Dean, 1974), was very high throughout the length of the core (Fig. 9A). The maximum LOI value was about 65% dry wt. at 16.5-17 cm and the minimum value was 28% at 7 cm.

There were three peaks of organic matter in the core from Crawford Lake: 1) 0-1 cm (surficial layer), 2) 15-18 cm, and 3) 33-48 cm respectively. There were two depth intervals, 2-15 cm and 20-33 cm, at which the organic matter content reached a minimum in the core (Fig. 9A).

Data from Lady Evelyn Reservoir (Fig. 9B) indicate a relatively low LOI. The maximum LOI value was about 35% dry wt. at 23.5 cm and the minimum value was 23% at 7.5 cm (Fig. 9B). There were two peaks in organic matter content in the core: one in the surficial layer (0-1 cm) and a second in the bottom layer (20-25 cm). The concentration of organic matter decreased upcore and reached its lowest value at 8 cm when it again began to increase.

The concentration of organic matter in the sediments ranged from 26% to 65% for Crawford Lake and 22% to 37% for Lady Evelyn Reservoir (Figs. 9A and 9B).

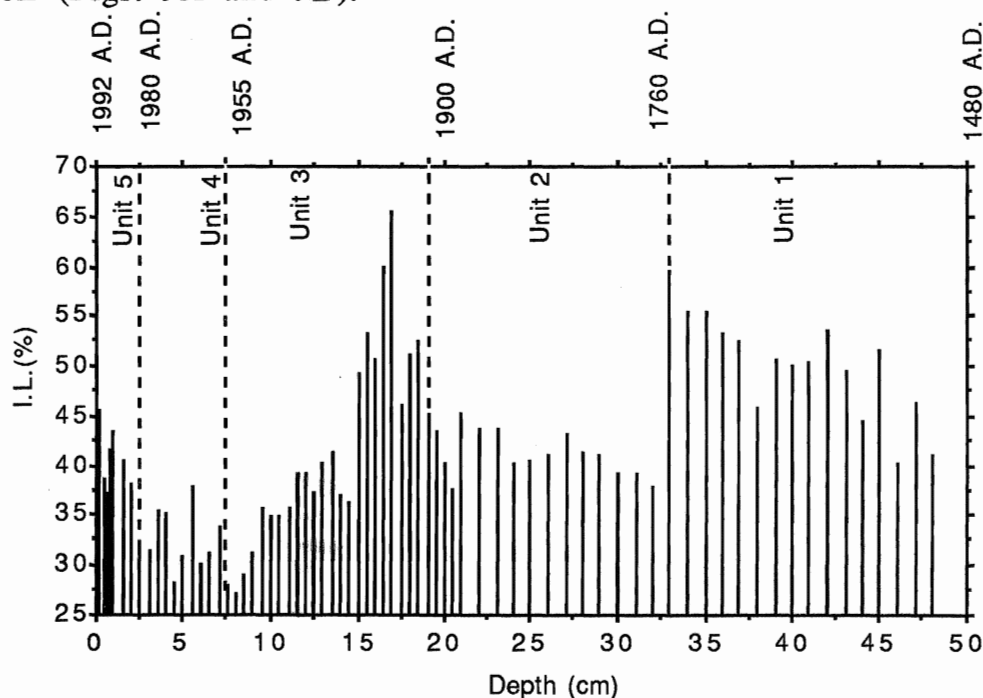


Fig. 9A. Stratigraphy of organic matter in the surficial sediments of Crawford Lake (April 8, 1992).



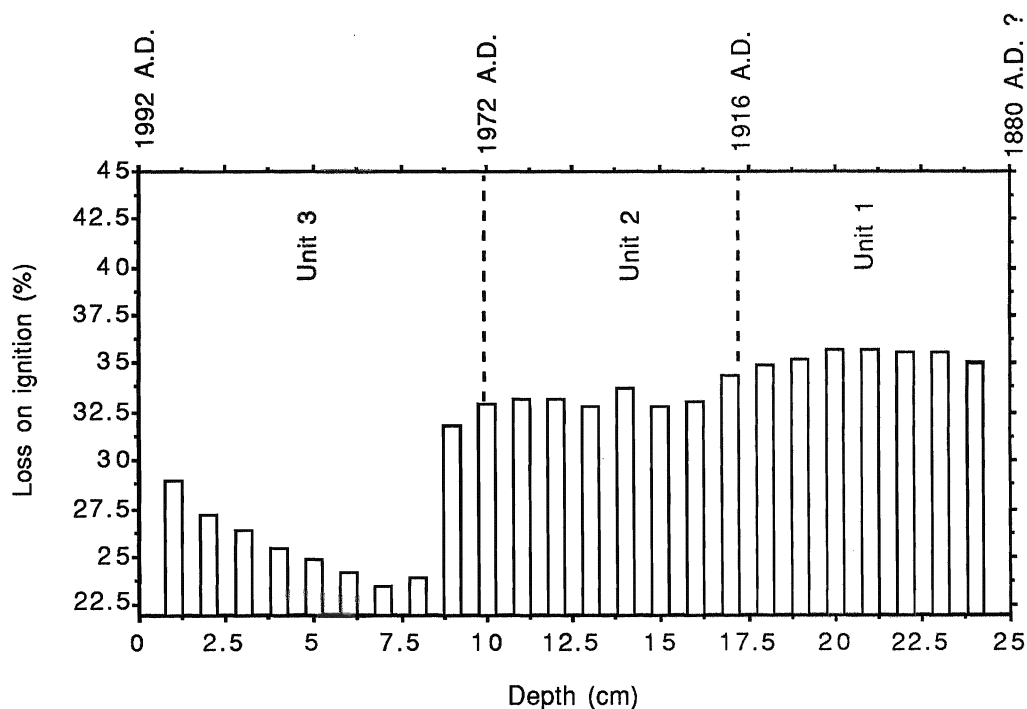


Fig. 9B. Stratigraphy of organic matter in the surficial sediments of KJ2 of Lady Evelyn Reservoir. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

*Production in Crawford Lake as accumulation rates of organic matter*

Production in Crawford Lake was associated with the rate of sedimentation of organic matter (Fig. 10). From 1480 to 1760 A. D. (Unit 1, 34-50 cm) the accumulation rates of organic matter in Crawford Lake was fairly constant and small, ranging from 18.8 to 26.0 g m<sup>-2</sup> yr<sup>-1</sup>. The accumulation rate decreased after 1760 A. D. and reached its lowest



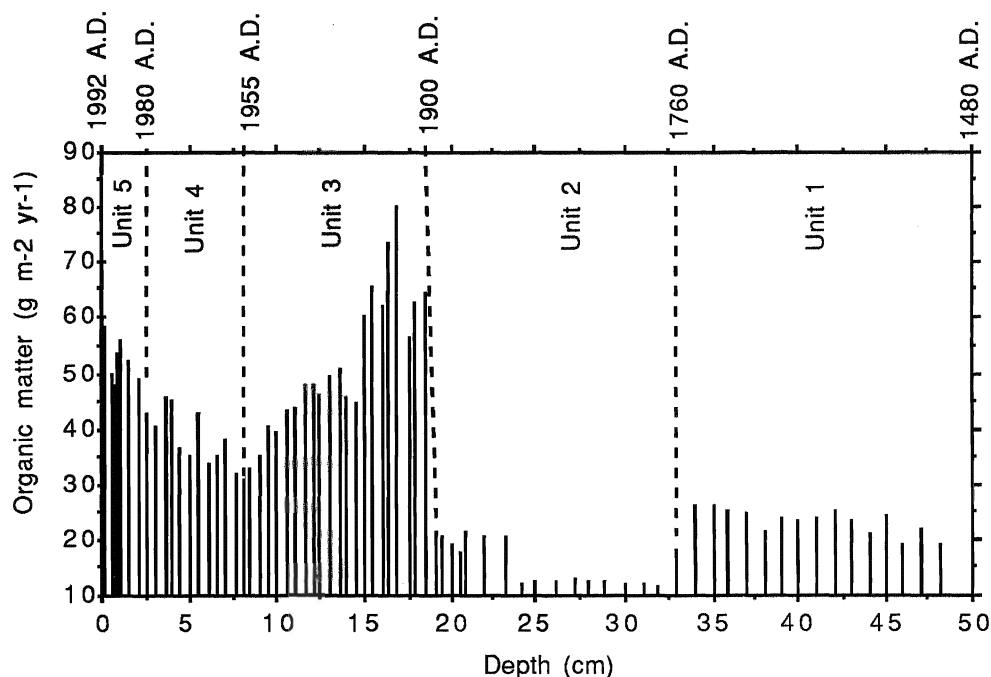


Fig. 10. Accumulation rates of organic matter in the surficial sediments of Crawford Lake.

level,  $11.4 \text{ g m}^{-2} \text{ yr}^{-1}$ , at 32 cm in Unit 2 (Fig. 10). A substantial increase in the accumulation rate of organic matter was observed between 15 and 18.5 cm. The highest accumulation rate ( $80.2 \text{ g m}^{-2} \text{ yr}^{-1}$ ) occurred at 17 cm. These depths (18.5-15 cm) represent the period ca. 1900-1920 A.D. After 1920 A. D. the accumulation rate of organic matter decreased until about 1955 A. D. when it again began to increase. During the past 40 years the accumulation of organic matter consistently increased upcore in the sediment core profile (Fig. 10).

#### *Stable isotopes of organic carbon in Crawford Lake*

The  $\delta^{13}\text{C}$  of organic carbon in the sediments of Crawford Lake ranged from  $-36.979$  to  $-27.861$  ‰ (Fig. 11). High values (as represented by high  $^{13}\text{C}$  content relative to  $^{12}\text{C}$ ) were found at 33-48 cm ( $-32.606$  -  $-27.861$  ‰). Very low values were found at

0-10 cm (-36.979 - -33.974 ‰). The interpretation of high and low  $\delta^{13}\text{C}$  values is provided in the discussion section.

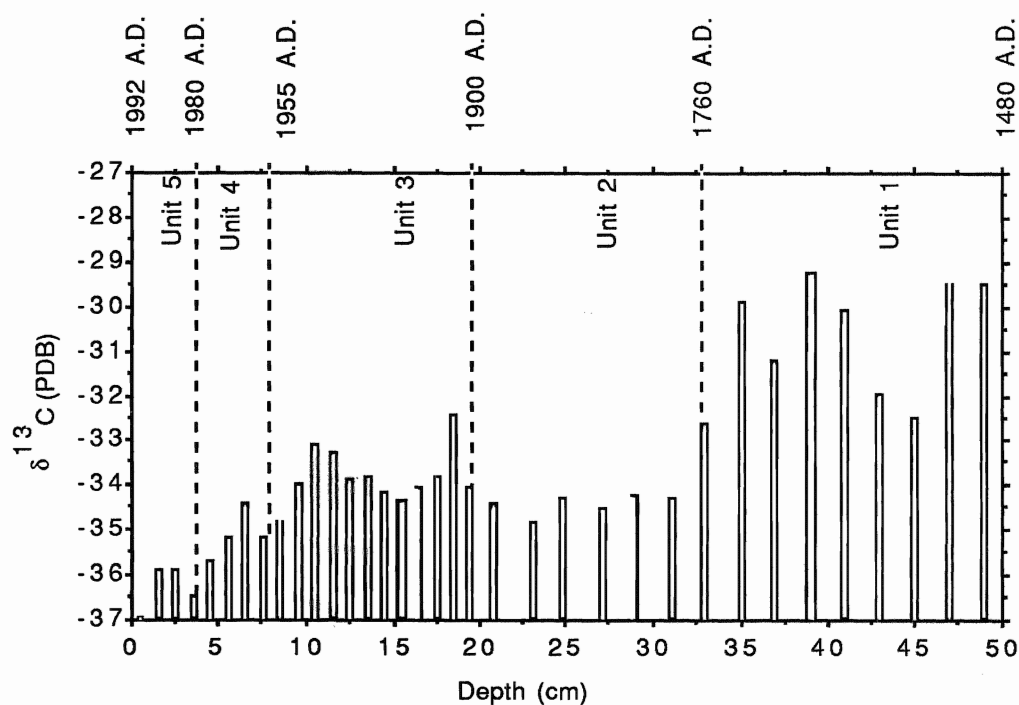


Fig. 11. Profile of  $\delta^{13}\text{C}$  of organic carbon in the surficial sediments of Crawford Lake.

### *Carbonates in Crawford Lake*

The carbonate content of the Crawford Lake core ranged from 0 to 47.2% (Fig. 12). Three peaks of carbonate content were found (3-9 cm, 19-32 cm and 41-48 cm).

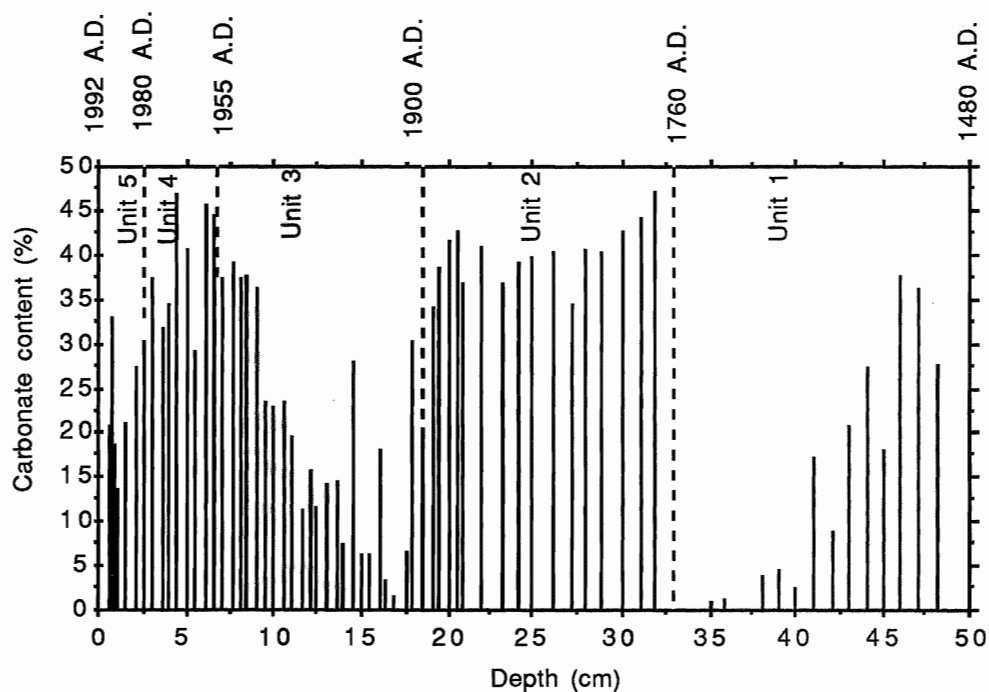


Fig. 12. Stratigraphy of carbonates in the surficial sediments of Crawford Lake.

Carbonate accumulation rates (Fig. 13) ranged from 0 to  $60.1 \text{ g m}^{-2} \text{ yr}^{-1}$  over the length of the core. During the first period (ca. 1480-1620 A.D) in Unit 1 (50-40 cm) the carbonate accumulation rate ranged from  $4.18$  to  $17.6 \text{ g m}^{-2} \text{ yr}^{-1}$ . The accumulation rate decreased after 1620 A.D. and was very low at 33-40 cm (ca. 1720-1620 A.D.). This constitutes the second period in Unit 1. A fair increase in the accumulation rate of carbonate was observed at 18.5-33 cm (ca. 1900-1760 A.D.) in Unit 2. From 1925 to 1970 A.D. (14-4.5 cm), the accumulation rate of carbonate consistently increased and became extremely high at 4.5-9.0 cm with values of  $30$ - $60 \text{ g m}^{-2} \text{ yr}^{-1}$ . In the past ten years the accumulation rate of carbonate has decreased. The reasons for the dramatic changes in carbonate accumulation rates are described in the discussion section of the thesis.

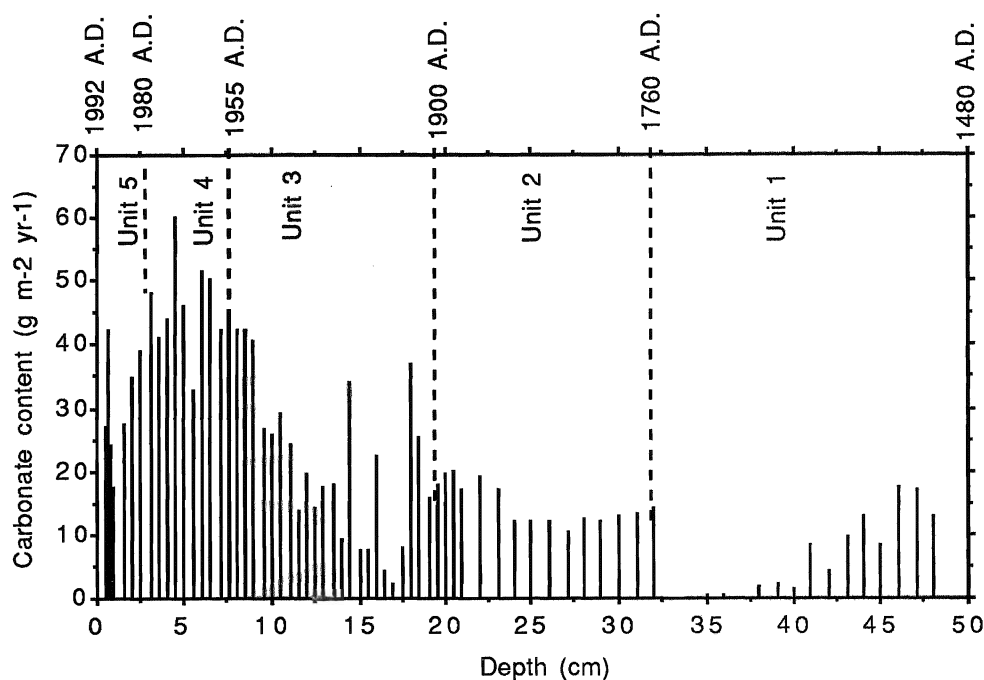


Fig. 13. Accumulation rates of carbonates ( $\text{g m}^{-2} \text{yr}^{-1}$ ) in the surficial sediments of Crawford Lake.

### *Carbonates in Lady Evelyn Reservoir*

Lady Evelyn Reservoir is located in a granitic basin (Ontario Hydro, 1989) while Crawford Lake is situated in a dolomite basin (Dickman, 1985). Carbonates in Lady Evelyn Reservoir were extremely low (0-5% dry wt.) and for this reason no figure was produced.

### *Comparison of the Mean Chlorophyll Derivatives in Crawford Lake and Lady Evelyn Reservoir*

The stratigraphy of chlorophyll derivatives (CD) occurs in a two stage pattern in Crawford lake (Fig. 14A). From 0 to 18.5 cm (Units 5, 4 and 3) the concentrations of CD were very high compared with the low values of samples from 18.5 to 50 cm (Units 2 and 1). Thus two distinct levels of CD occurred in the top 50 cm of sediment in Crawford Lake.

The stratigraphy of chlorophyll derivatives (CD) of the core from Lady Evelyn Reservoir (Fig. 14B) indicates that from the bottom (25 cm) to 10 cm (Units 1 and 2) the concentration of chlorophyll derivatives was almost constant, ranging from 3.0 to 3.5 SPU/O.M.(g). From this depth, CD began to increase to 2 cm and then decreased at the surface layer.

In the core of Crawford Lake from the surface to 18.5 cm (Units 5, 4 and 3), two chlorophyll derivative peaks were found (2 cm and 12.5 cm). In 18.5-50 cm (Units 2 and 1) Chlorophyll derivatives increased in concentration at 26 cm and 43 cm (Fig. 14A).

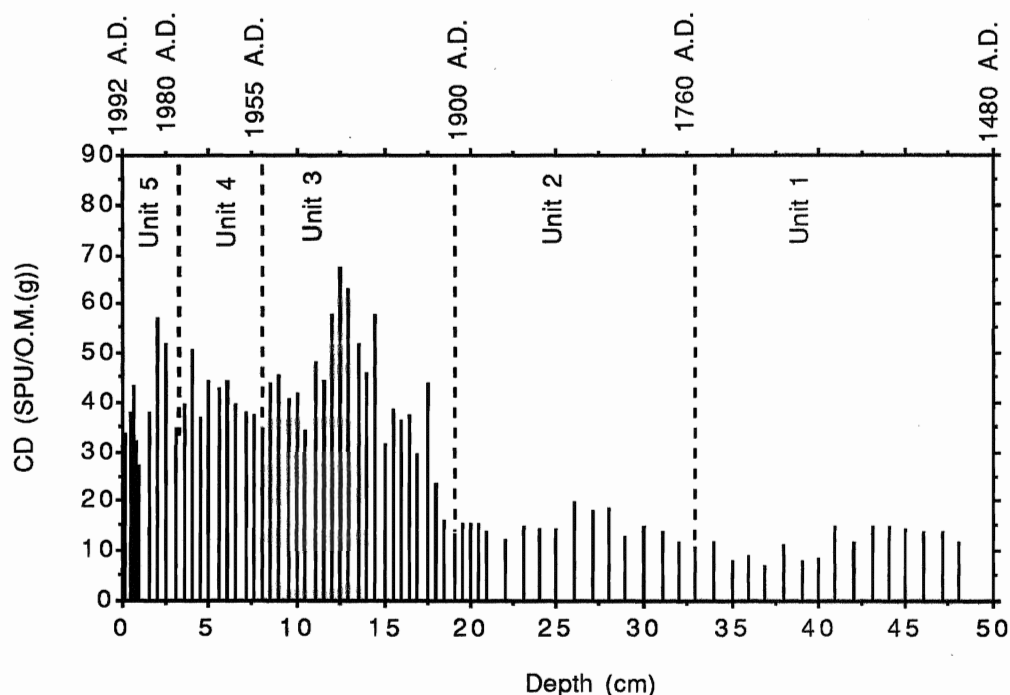


Fig. 14A. Stratigraphy of chlorophyll derivatives (SPU/O.M.(g)) in the surficial sediments of Crawford Lake.

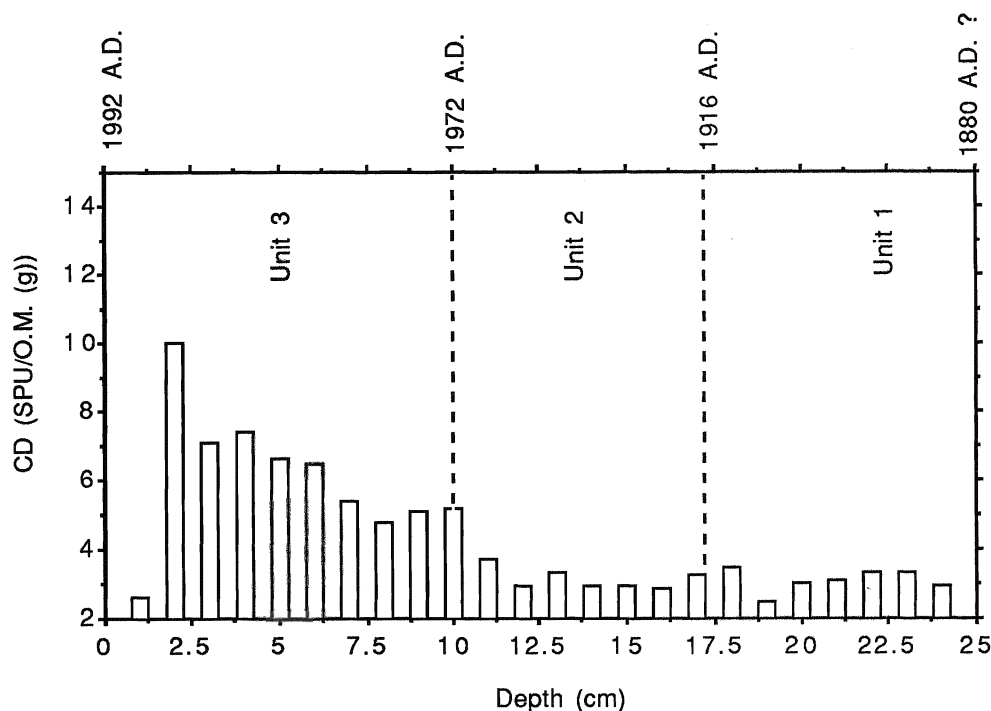


Fig. 14B. Stratigraphy of chlorophyll derivatives (SPU/O.M.(g)) in the surficial sediments of Lady Evelyn Reservoir. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

In Crawford Lake, the accumulation rate of chlorophyll derivatives was calculated by using the formula described in the methods section. CD accumulation rates ranged from 0.015 to 0.31 SPU cm<sup>-2</sup> yr<sup>-1</sup> (Fig. 15). During the period between 1480 to 1900 A. D. (Units 2 and 1) only 0.016-0.035 SPU cm<sup>-2</sup> yr<sup>-1</sup> (at the depths of 50-18.5 cm) was observed. However, from 18.5 cm (which corresponds to ca. 1900 A. D.) a substantial increase in the accumulation of these pigments was observed. This trend was closely correlated with the increasing rate of deposition of organic matter (Fig. 10) as previously noted. The highest level of accumulation of chlorophyll derivatives occurred at 13 cm (0.31 SPU cm<sup>-2</sup> yr<sup>-1</sup>). From 13 cm to

6.5 cm (ca. 1920-1955 A. D.), the accumulation rate continuously decreased to  $0.14 \text{ SPU cm}^{-2} \text{ yr}^{-1}$ . Then at 6.5 cm it began to increase upcore to the surface.

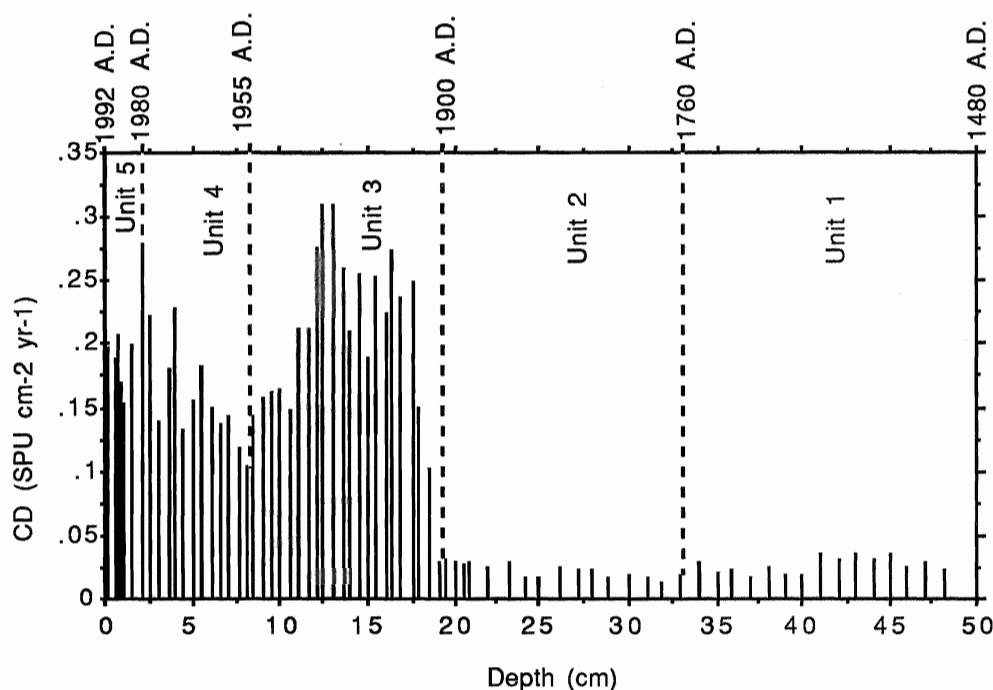


Fig. 15 Accumulation of chlorophyll derivatives ( $\text{SPU cm}^{-2} \text{ yr}^{-1}$ ) in the surficial sediments of Crawford Lake.

### *Native chlorophylls in Crawford Lake and Lady Evelyn Reservoir*

Native chlorophylls refers to that part of the chlorophyll that was not degraded (Swain, 1985). As a result, native chlorophylls can be used as an index of relative sediment core pigment preservation. Native chlorophylls increased in concentrations at five depths in the Crawford Lake core, the surface layer (0-2 cm), 5-10 cm, 18.5-21 cm, 36 cm, and at 48 cm (Fig. 16A).

In comparison with Crawford Lake, the concentration of native chlorophylls in the sediments of Lady Evelyn Reservoir was relatively

low (Fig. 16B) as preservation of pigments in Lady Evelyn Reservoir was poor except in the surficial layer. The increase in native chlorophylls in the early 1900's was probably caused by the high accumulation rate which occurred after the dam was built in 1916. The reasons for this will be described in the discussion section of this thesis.

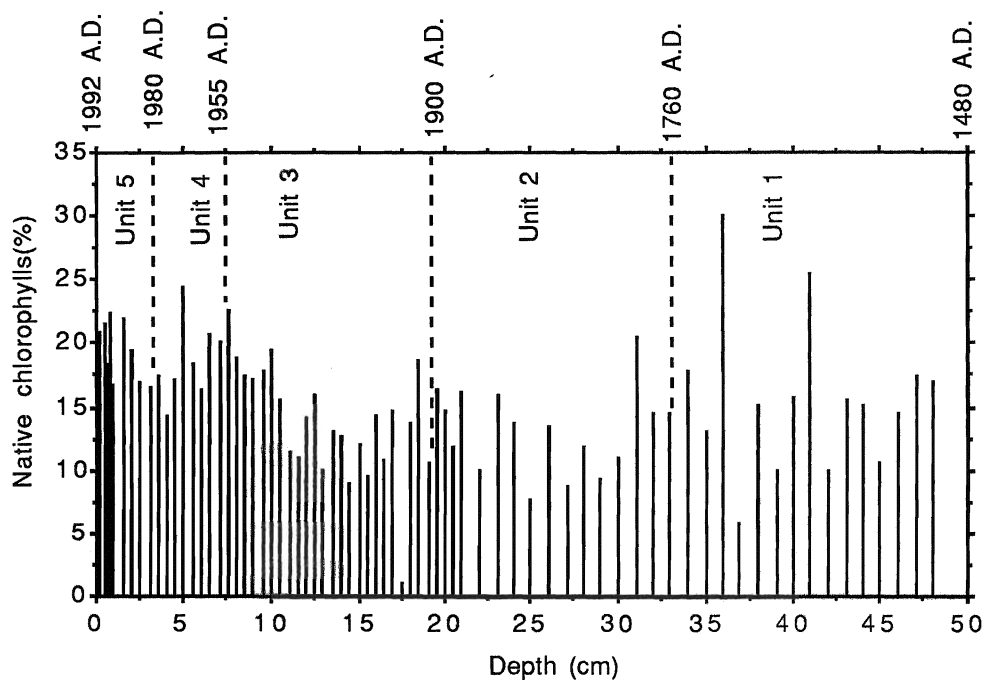


Fig. 16A. Stratigraphy of native chlorophylls in the surficial sediments of Crawford Lake. Native chlorophylls is expressed as a percentage (%) of the chlorophyll derivatives.



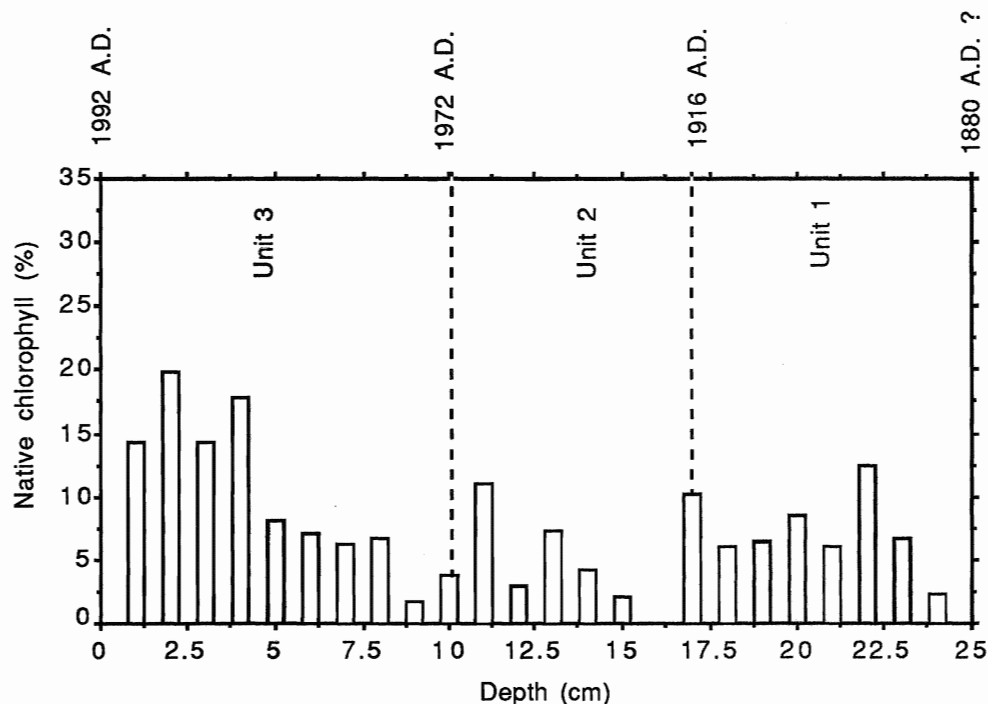


Fig. 16B. Stratigraphy of native chlorophyll in the surficial sediments of Lady Evelyn Reservoir. Native chlorophylls is expressed as a percentage (%) of the chlorophyll derivatives. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

### ***Total carotenoids in Crawford Lake and Lady Evelyn Reservoir***

The temporal trend in total carotenoids (TC) in the Crawford Lake core (Fig. 17A) was similar to the trend in chlorophyll derivatives (Fig. 14A). There was a distinct boundary which separated the core into two different sections. From the surface to 18.5 cm (1992-1900 A. D., i.e. Units 5, 4 and 3) the concentrations of TC were very high. From 18.5 to 50 cm (1900-1480 A. D., i.e. Units 2 and 1) TC was extremely low. The reasons for this are provided in the discussion section of this thesis.

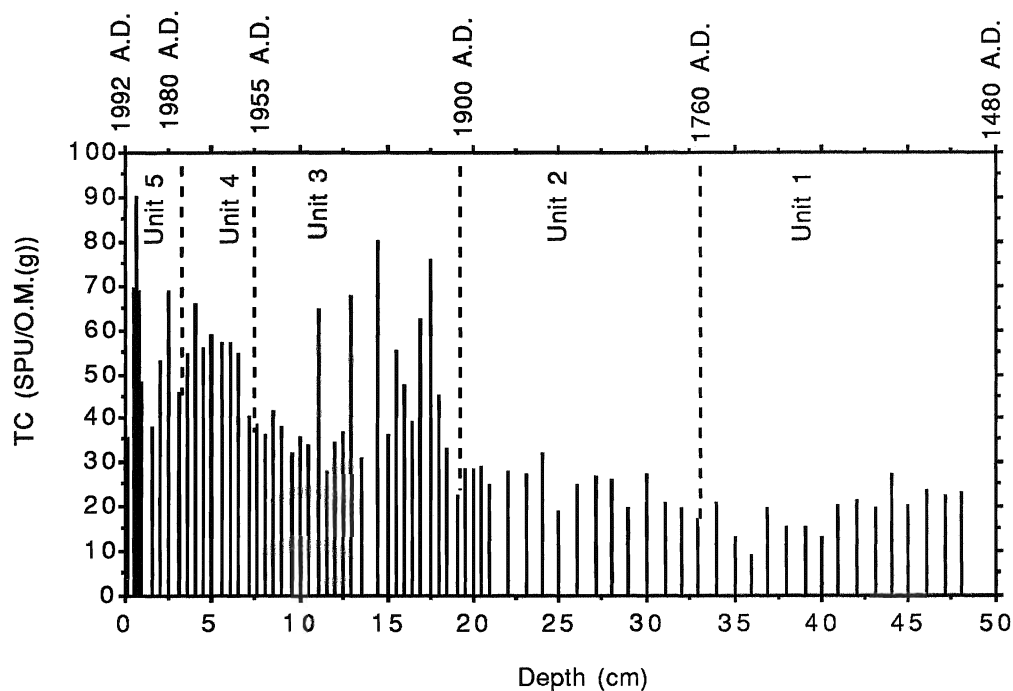


Fig. 17A. Stratigraphy of total carotenoids (SUP/O.M. (g)) in the surficial sediments of Crawford Lake.

The concentration of total carotenoids did not change substantially from 25 cm to 10 cm (Units 1 and 2), ranging from 0.75 to 1.5 SPU/O.M.(g) in Lady Evelyn Reservoir (Fig. 17B). It began to increase from 8 cm to 2 cm (within Unit 3) and then dramatically decreased in the surface layer (Fig. 17B).

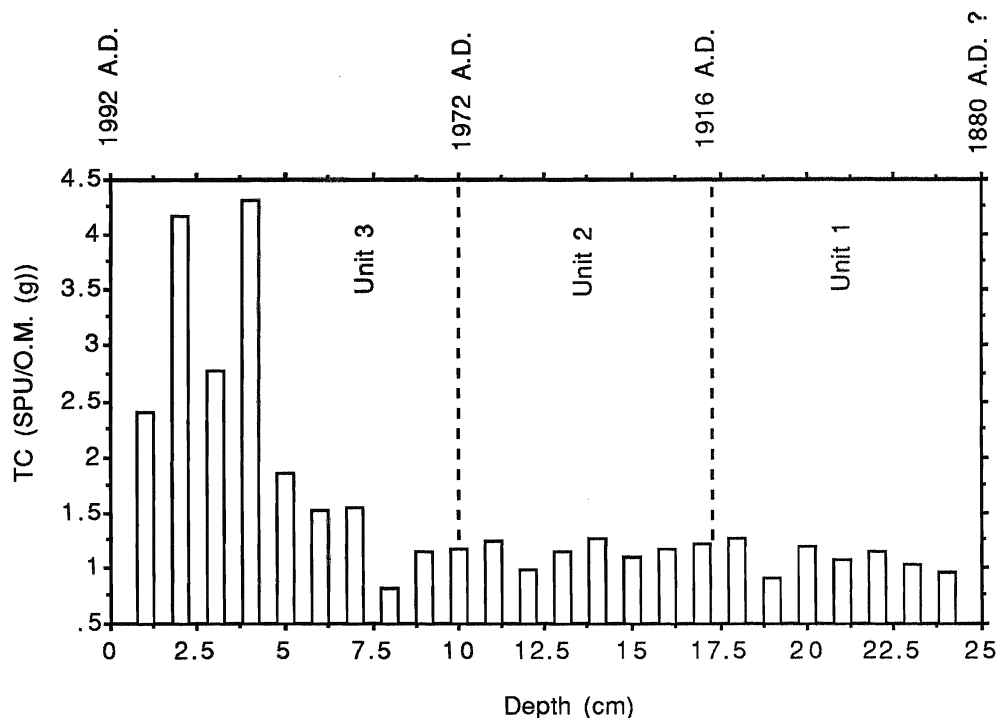


Fig. 17B. Stratigraphy of total carotenoids (SPU/O.M.(g)) in the surficial sediments of Lady Evelyn Reservoir. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

The accumulation rates of total carotenoids were from 0.02 to 0.50 SPU cm<sup>-2</sup> yr<sup>-1</sup> in the Crawford Lake core (Fig. 18). During the period between 1480 A. D. and 1900 A. D. (Units 2 and 1) the accumulation rates were very low, ranging from 0.02 to 0.05 SPU cm<sup>-2</sup> yr<sup>-1</sup>. This is similar to the pattern for the chlorophyll derivatives which also displayed very low values in this period (Fig. 18). The accumulation rate of TC began to increase at 18.5 cm and continued to increase to 17 cm (ca. 1910 A.D.). Then during the subsequent 45 years (8-17 cm of Unit 3), the deposition of TC underwent frequent fluctuations, but displayed an overall decline (Fig. 18). The accumulation rate reached its lowest level (0.11 SPU cm<sup>-2</sup> yr<sup>-1</sup>) at 7 cm (ca. 1950 A. D.). After circa 1955 A. D.

(Unit 4), however, the accumulation rate of total carotenoids increased again with a peak at 1 cm (ca. 1978 A. D.) that approached the maximum accumulation rate at 18.5 cm (ca. 1900 A. D.) (Fig. 18).

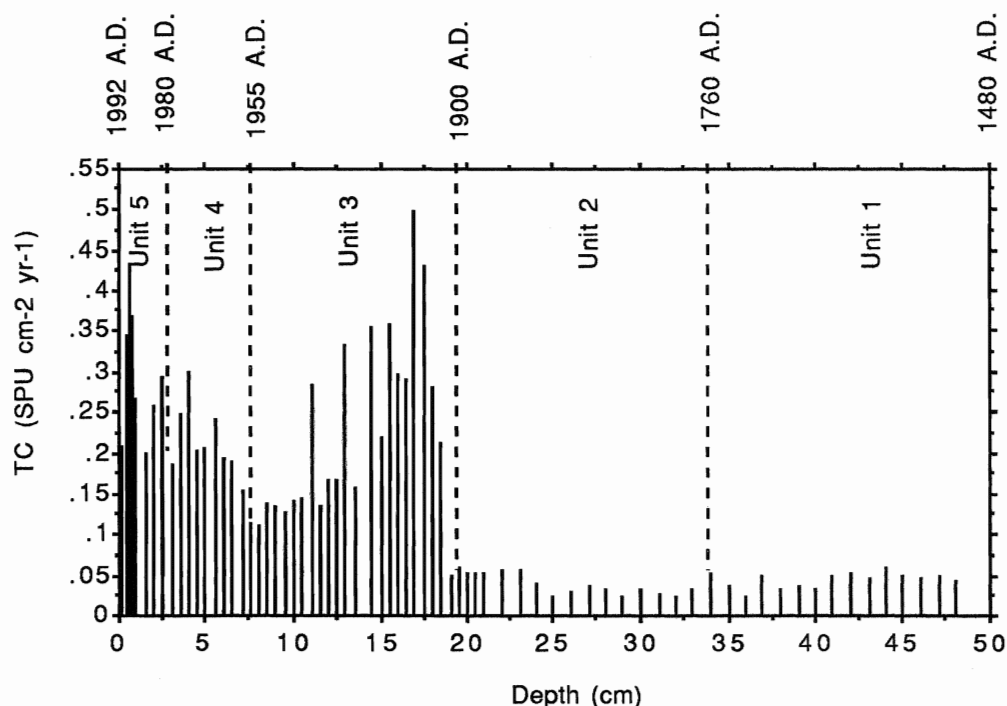


Fig. 18. Accumulation rates of total carotenoids ( $\text{SPU cm}^{-2} \text{yr}^{-1}$ ) in the surficial sediments of Crawford Lake.

#### *Ratio of chlorophyll derivatives to total carotenoids (CD/TC)*

Because carotenoids are degraded faster than chlorophylls (Swain, 1985) the CD/TC ratio can be used to show how well preserved the pigments are in the sediments. The CD/TC ratio was high at depths of 0 cm, 1.5-2 cm, 9.5-10 cm, 25-26 cm and 36 cm in Crawford Lake (Fig. 19A), indicating poor pigment preservation at these times.

The value of CD/TC ranges from 0.5 to 10 (Fig. 19B) in Lady Evelyn Reservoir and was very high and variable compared with that of Crawford Lake (Fig. 19A).

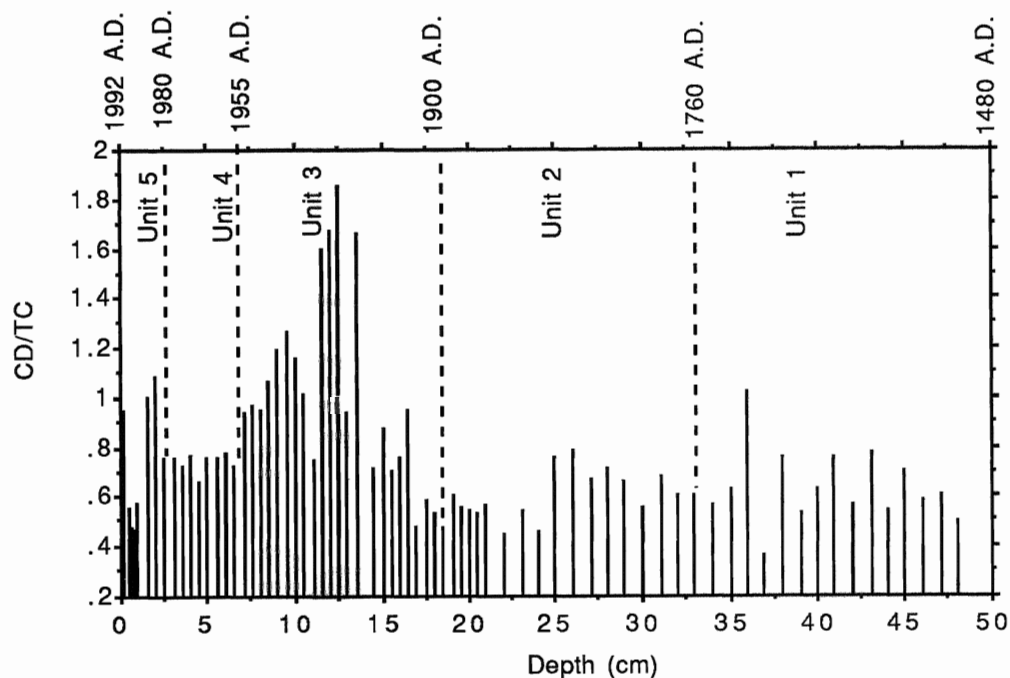


Fig. 19A. The ratio of chlorophyll derivatives to total carotenoids in the surficial sediments of Crawford Lake

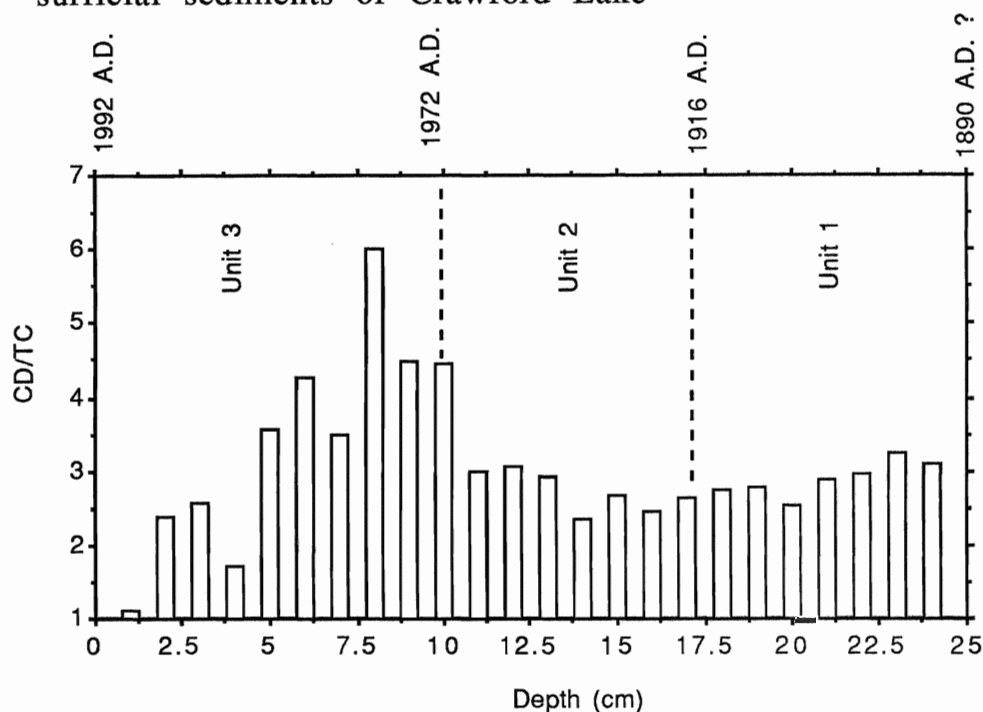


Fig. 19B. The ratio of chlorophyll derivatives to total carotenoids in the surficial sediments in Lady Evelyn reservoir. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

### *Bacteriochlorophyll pigments*

The stratigraphy of bacteriochlorophyll followed the same trend as the chlorophyll derivatives (Fig. 14A), with high values at 2 cm and 12.5 cm in the upper part of the core (0-18.5 cm, i.e. Units 5, 4 and 3) (Fig. 20). In the brownish green coloured lower section of the core (18.5-50 cm, i.e. Units 2 and 1) minor peaks occurred at 26 and 43 cm.

The accumulation rates of bacteriochlorophyll pigments ranged from 0.01 to 0.31  $\mu\text{g cm}^{-2} \text{yr}^{-1}$  (Fig. 21). At the depths of 18.5-50 cm (Units 1 and 2, ca. 1900-1480 A.D.), the accumulation rate of bacteriochlorophyll was very low, only 0.01-0.015  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ . In the upper section of the core (Units 5, 4 and 3), which was a dark grey colour, the accumulation rate of the pigments was extremely high, 0.08-0.35  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ . From 1900 A.D. (18.5 cm), the accumulation rate of bacteriochlorophyll began to increase and reached peak values of 0.25  $\mu\text{g cm}^{-2} \text{yr}^{-1}$  at 13 cm (ca. 1930 A.D.). Then during the subsequent 25 years (1930-1955 A.D.) a decline in the accumulation rates of bacteriochlorophyll occurred (Fig. 21). From 7.5 cm (1955 A.D.) to 3 cm (1980 A.D.), the accumulation rate began to increase again. At 2.5 cm, the accumulation rate reached a peak of about 0.35  $\mu\text{g cm}^{-2} \text{yr}^{-1}$  and then declined to its present value of about 0.20  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ . After 1980 A. D. (0-3 cm, Fig.21), the accumulation rate for bacterial pigments fluctuated between 0.25 and 0.17  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ (Fig. 21).

No bacteriochlorophyll was found in the sediments of Lady Evelyn Reservoir because the hypolimnion of this reservoir was not anaerobic for sufficient periods of time to permit phototrophic bacteria such as *Chlorobium* species to colonize the area.

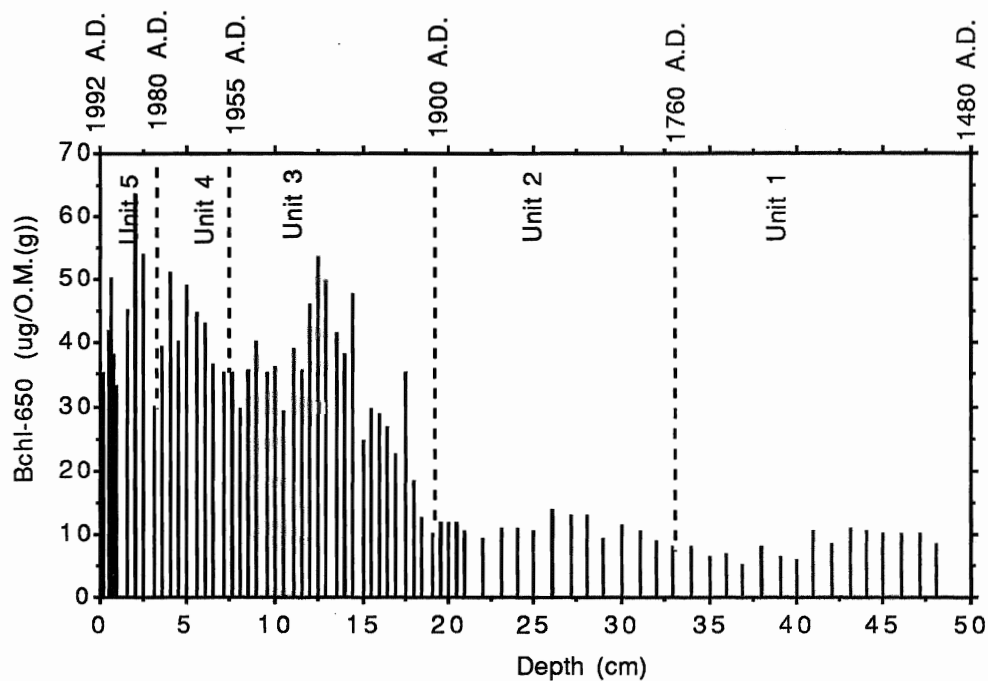


Fig. 20. Stratigraphy of *Chlorobium* chlorophyll ( $\mu\text{g/O.M. (g)}$ ) in the surficial sediments of Crawford Lake.

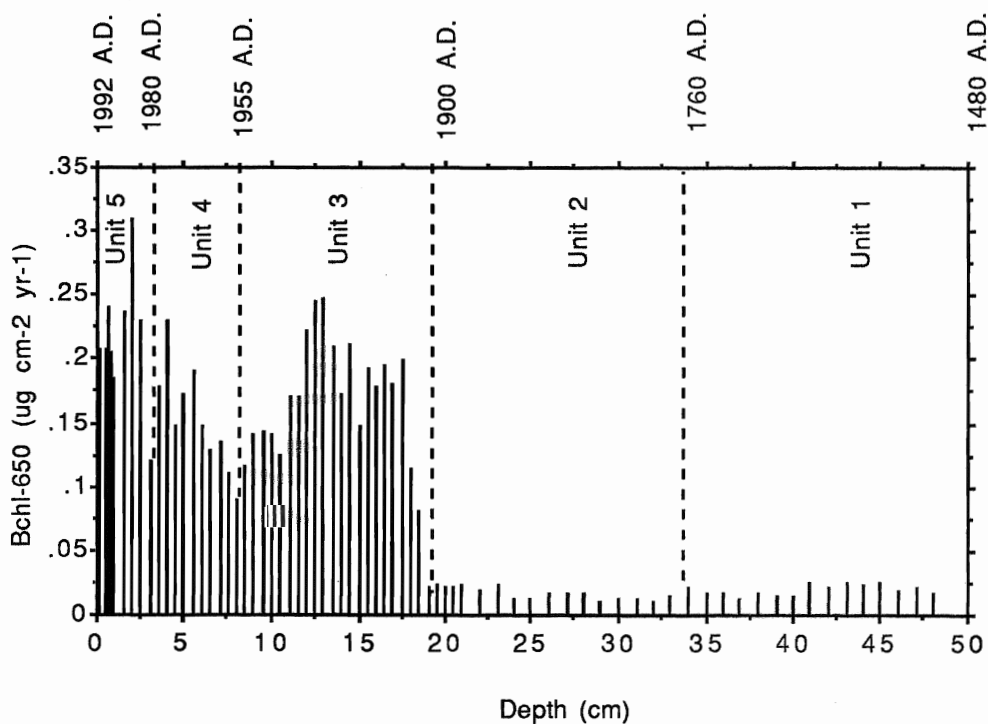


Fig. 21. Accumulation rates of bacteriochlorophyll ( $\mu\text{g cm}^{-2} \text{yr}^{-1}$ ) in the surficial sediments of Crawford Lake.

## *Oscillaxanthin*

The concentration of oscillaxanthin was very high in the lower part of the Crawford Lake core. This part of the core exhibited a brownish grey colour (Units 2 and 1, Fig. 22A). Oscillaxanthin was very low in the upper part of the core (Units 5, 4 and 3).

In the upper part of the core (Units 5, 4 and 3), two small peaks in oscillaxanthin were found at 4 cm and 8 cm (within Unit 4). Major peaks occurred in the lower part of the core (Units 2 and 1) at 17, 21, 34, 37 and 44 cm (Fig. 22A).

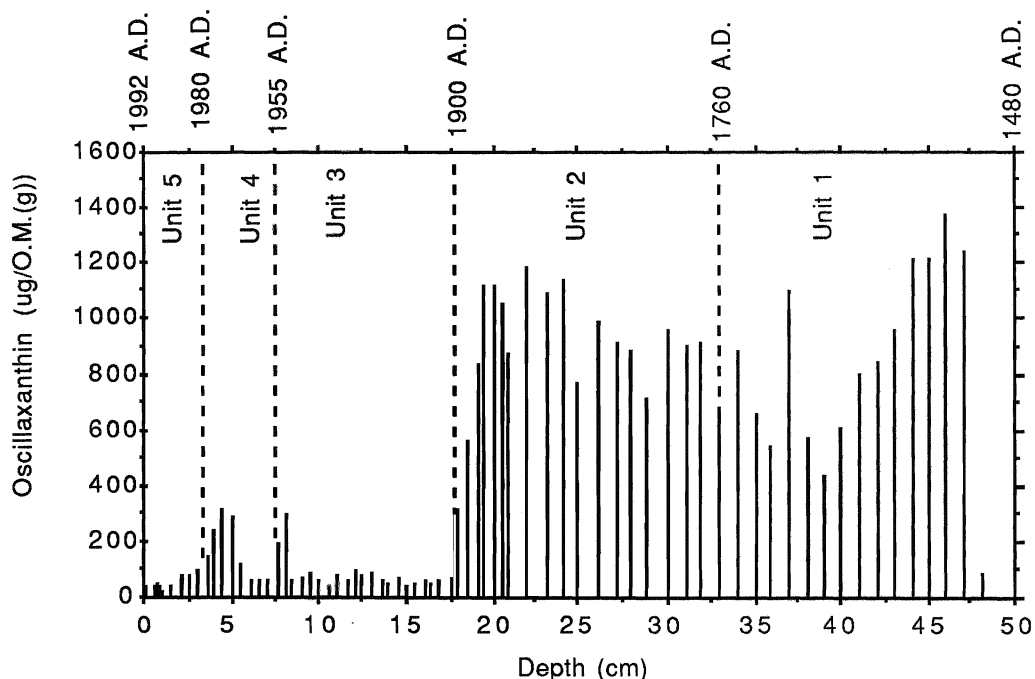


Fig. 22A. Stratigraphy of oscillaxanthin ( $\mu\text{g/O.M. (g)}$ ) in the surficial sediments of Crawford Lake

The concentration of oscillaxanthin in Lady Evelyn Reservoir ranged from 5 to 40  $\mu\text{g/O.M. (g)}$  (Fig. 22B), which was very low compared with the value in Crawford Lake (50-1,400  $\mu\text{g/O.M. (g)}$ ) (Fig. 22A).



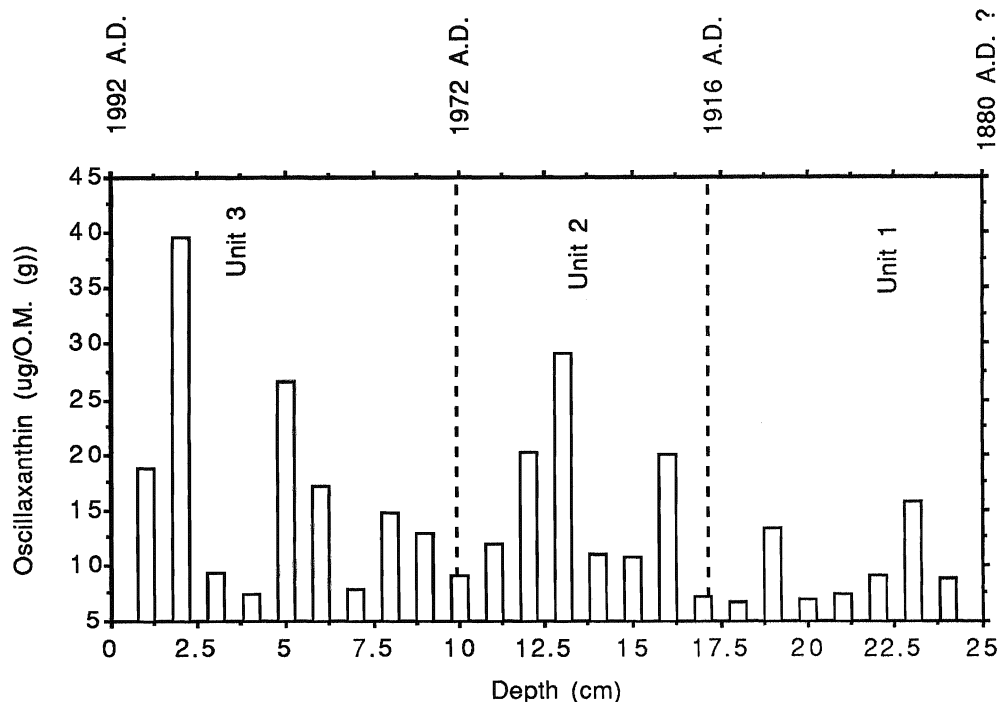


Fig. 22B. Stratigraphy of oscillaxanthin ( $\mu\text{g}/\text{O.M. (g)}$ ) in the surficial sediments of Lady Evelyn Reservoir. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

In my oscillaxanthin pigment profile from Crawford Lake (Fig. 23) the accumulation rate of oscillaxanthin ranged from 0.15 to  $0.35 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ . There are two very different periods of accumulation, 1480-1900 A.D. and 1900-1992 A.D (Fig. 23). From 18.5 to 50 cm (Units 2 and 1, ca. 1900-1480 A.D.), the accumulation rate of oscillaxanthin was very high. Otherwise it showed low levels at 0-18.5 cm (Units 5, 4 and 3). Three trends in increasing levels of oscillaxanthin were noted during the first period (1480-1900) in 1480-1550 A.D. (50-45 cm), 1635-1665 A.D. (39-37 cm) and 1765-1905 A.D. (13-8.5 cm). In addition there were three peaks in the upper part of the core at 4.5 cm (1970 A.D.), 8 cm (1955 A.D.) and 12 cm (1935 A.D.).

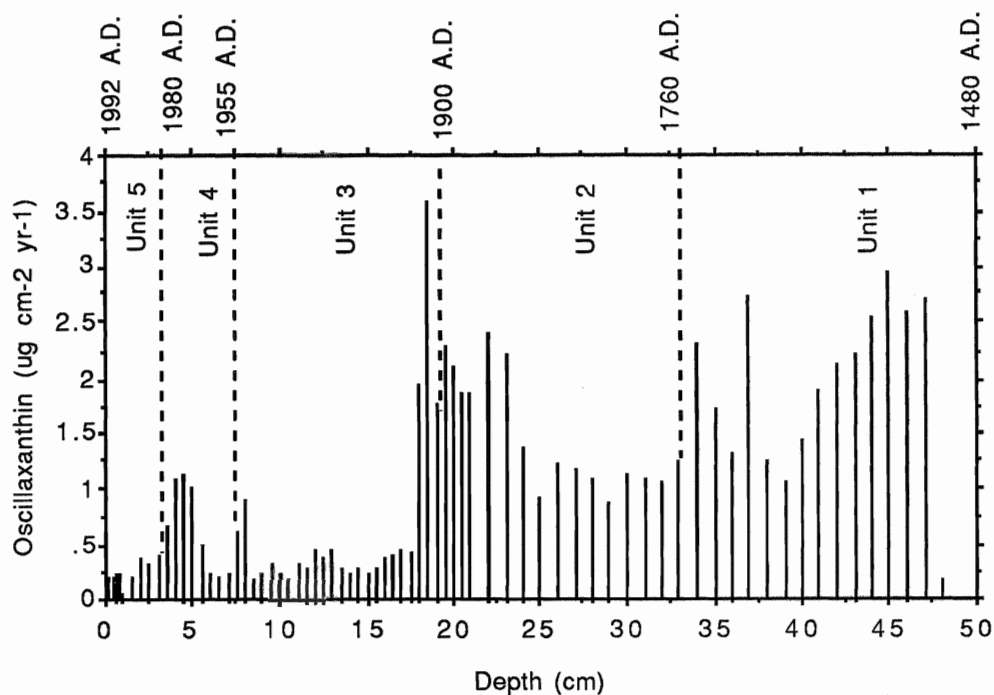


Fig. 23. Accumulation rates of oscillaxanthin ( $\mu\text{g cm}^{-2} \text{yr}^{-1}$ ) in the surficial sediments of Crawford Lake.

### *Myxoxanthophyll*

The temporal trend in myxoxanthophyll in Crawford Lake (Fig. 24A) was similar to the trend in oscillaxanthin (Fig. 22A). The concentrations of myxoxanthophyll are very high at 18.5-50 cm and low in the upper part of the core (0-18.5 cm, Units 5, 4 and 3). The reasons for this are discussed in the next section.

The concentration of myxoxanthophyll in Lady Evelyn Reservoir ranged from 2 to 9  $\mu\text{g/O.M. (g)}$  (Fig. 24B), which was very low compared to the values in Crawford Lake (50-550  $\mu\text{g/O.M. (g)}$ ) (Fig. 24A).

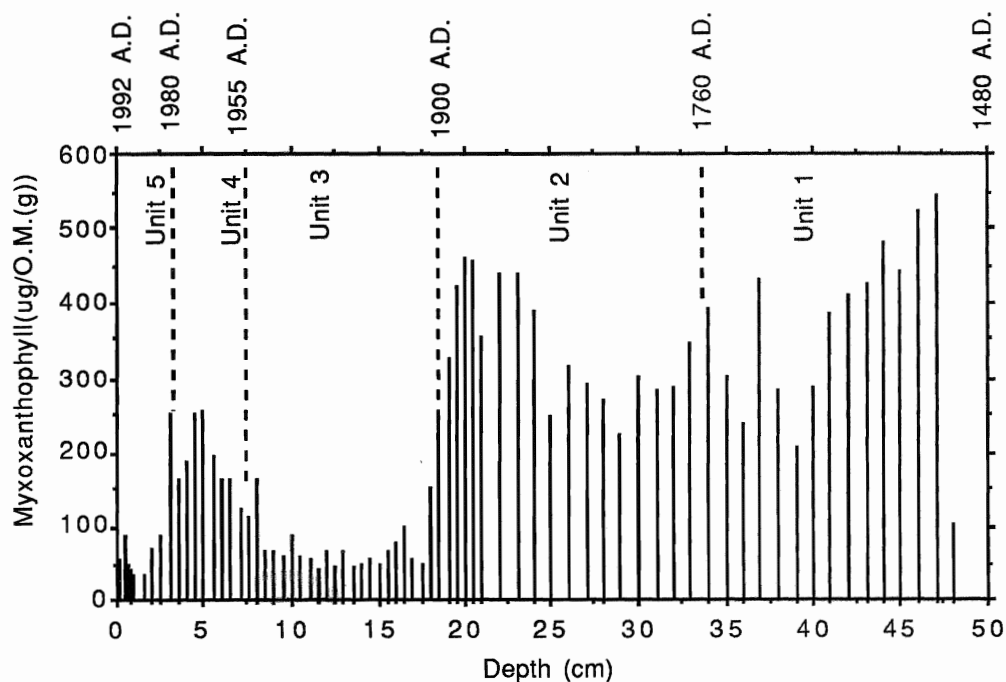


Fig. 24A. Stratigraphy of myxoxanthophyll ( $\mu\text{g}/\text{O.M. (g)}$ ) in the surficial sediments of Crawford Lake

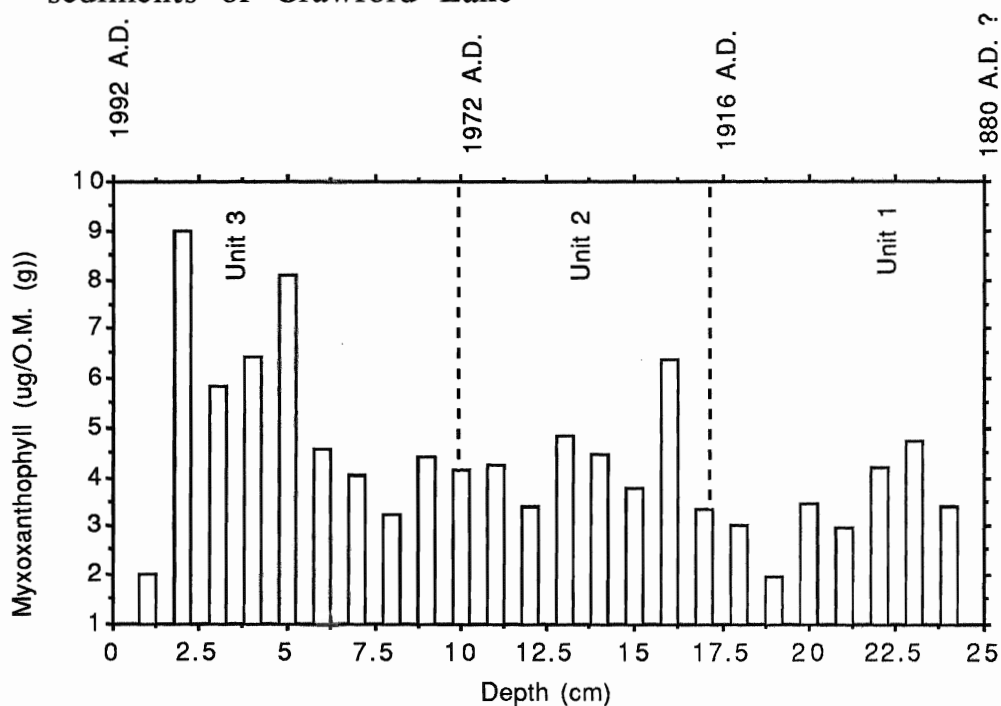


Fig. 24B. Stratigraphy of myxoxanthophyll ( $\mu\text{g}/\text{O.M. (g)}$ ) in the surficial sediments of Lady Evelyn Reservoir. Bars represent continuous depth of sediment samples from 0-1 cm (first layer) to 23-24 cm (bottom layer).

Three periods of high rates of sedimentation were noted in the Crawford Lake core, i.e. 1978-1955 A.D. (8-3 cm), 1860-1900 A.D. (24-18.5 cm) and 1520-1705 A.D. (47-34 cm) (Fig. 25).

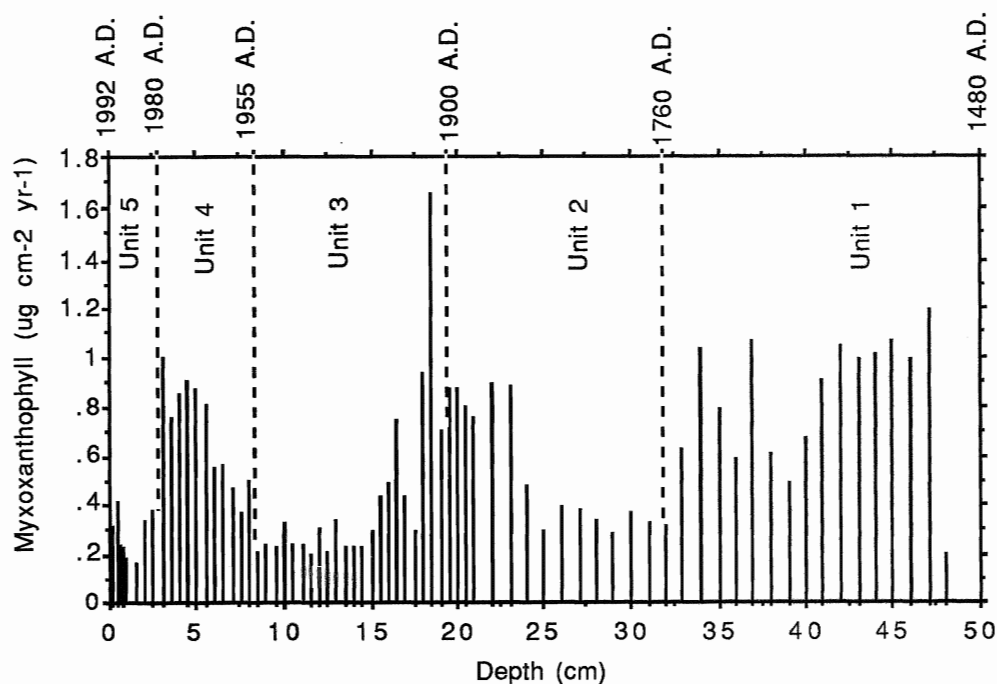


Fig. 25. Accumulation rates of myxoxanthophyll ( $\mu\text{g cm}^{-2} \text{yr}^{-1}$ ) in the surficial sediments of Crawford Lake.

### *Ratio of oscillaxanthin to myxoxanthophyll*

The ratio between oscillaxanthin and myxoxanthophyll (Osc/Myx) appears to be a degradation-immune indicator of the relative production of the two pigments (Sanger, 1988). A stratigraphic shift in Osc/Myx values indicates a change in the proportion of *Oscillatoriaceae* in the blue-green algae of a lake (Sanger, 1988).

Two different sections can be distinguished in the core, i.e. from 0 to 18.5 cm (Units 5, 4 and 3) and 18.5 to 50 cm (Units 2 and 1). Very different values of Osc/Myx occur in each of these sections (Fig. 26). In the upper part of the core the ratio of Osc/Myx is low, ranging from 0.34 to 1.8. In the lower part the ratio is very high (2.1-3.3).

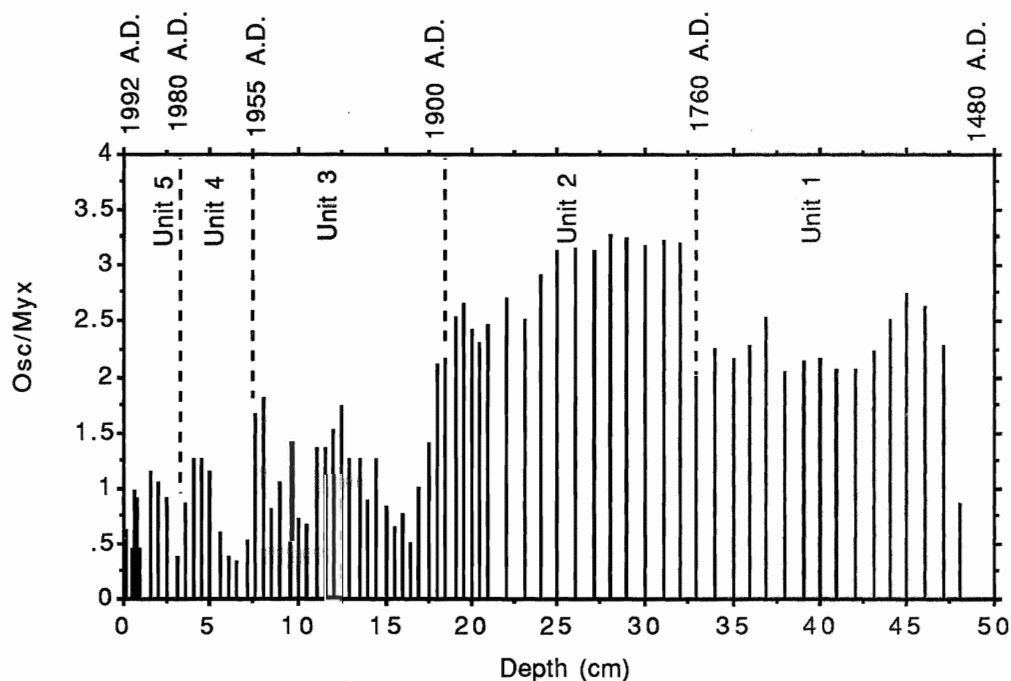


Fig. 26. Downcore ratio of oscillaxanthin to myxoxanthophyll in the surficial sediments of Crawford Lake.

#### *Pigment Analysis of the Crawford Lake algal mats*

The results of the algal mat pigment analysis, i.e. chlorophyll derivatives (CD), native chlorophylls (NC), total carotenoids (TC), Oscillaxanthin, and Myxoxanthophyll, are presented in Table 5.

The concentrations of all of these pigments were fairly low in the mixolimnion cores compared with those of the monimolimnion core. The algal mat displayed very high pigment concentrations.

The ratios of oscillaxanthin to myxoxanthophyll are higher than the ratios in the upper layer (0-18 cm) of the monimolimnion core and about the same values as those in the lower part of the long core (below 18 cm).

Table 5. Pigment concentrations in the Crawford Lake chemocline cores

No. of core	Depth (cm)	CD (SPU/ O.M.(g))	TC (SPU/ O.M.(g))	NC (%)	Osc. ( $\mu$ g/O.M.(g))	Myx. ( $\mu$ g/O.M.(g))	Osc./ Myx
Core 1	0-1	3.7	5.7	15. 9	31.2	10.4	3.0
	1-2	3.4	4.0	15. 8	28.5	9.7	2.9
	2-3	3.2	5.1	13. 1	20.3	9.5	2.1
	9-10	2.8	5.2	10. 0	23.8	9.8	2.4
Dark Algal mat	0-0.2	46.0	10.9	60. 3	279.6	158.6	1.8
light coloured marl layer +seston	0.2-0.4	9.3	18.1	15. 7	49.7	39.8	1.2

## Discussion

The sediment core from the monimolimnion of Crawford Lake was composed of two distinct layers, dark grey upper layer (0-18 cm, ca. 1900-1992 A. D.) and a brownish grey lower layer (18-50 cm, 1500-1900 A. D.). Each of these two layers are made up of well laminated and poorly laminated sublayers. I have characterized the top layer (0-18 cm) as representing a nutrient-rich (eutrophic) period in which phytoplankton and phototrophic bacteria were abundant in Crawford Lake. The bottom layer (18-50 cm) was characterized by a dense benthic cyanophyte "carpet" (Fig. 27) and good preservation of blue-green algal pigments (especially oscillaxanthin). The presence of *Oscillatoria* and *Lyngbya* etc. in Crawford Lake at 12 to 14 m (Dickman, unpublished report) (Fig. 27) was the primary source of oscillaxanthin and myxoxanthophyll in the Crawford Lake core (Dickman and Han, in prep.). The bottom layer (18-50 cm) in the Crawford Lake

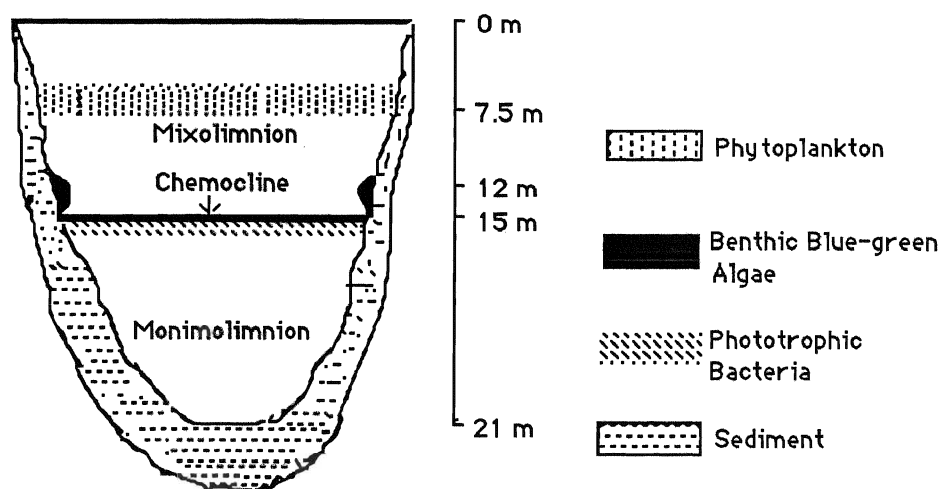


Fig. 27. A schematic diagram representing the locations of the majority of the phototrophic bacteria and benthic blue-green algae in Crawford Lake, Ontario

monimolimnion core was associated with a relatively low standing crop of algae and phototrophic bacteria, low sedimentation rates and abundant pine needles. Sedimentation rate estimates were based on my  $^{210}\text{Pb}$ , and  $^{137}\text{Cs}$  data. In addition, the sedimentation rates were estimated directly by counting the varves in the core (Boyko, 1978; Dickman, 1985 and Rybak & Dickman, 1987).

In order to establish the eutrophication history of the Crawford Lake, it is very important to study the chronology of the core. By lamina counting, the sedimentation rates were estimated at  $2.2 \text{ mm yr}^{-1}$  from 1978 to 1992 and  $2.0 \text{ mm yr}^{-1}$  from 1954 to 1978. The sedimentation rates (Table 3) which were derived from  $^{210}\text{Pb}$  dating methods were comparable with those obtained by the lamina counting methods. The sedimentation rate was high at 0-5 cm with an average value of  $2.21 \text{ mm yr}^{-1}$ . At 5-7 cm the sedimentation rate decreased to  $1.65 \text{ mm yr}^{-1}$ . It increased at 9-12.5 cm ranging from 1.65 to  $2.25 \text{ mm yr}^{-1}$  and decreased again at 12.5-18.5 cm ranging from 1.25- $1.77 \text{ mm yr}^{-1}$ .

The sedimentation rate of  $1.38 \text{ mm yr}^{-1}$  estimated by  $^{137}\text{Cs}$  above the depth of 4 cm was low compared to the average rate estimated by  $^{210}\text{Pb}$  ( $2.21 \text{ mm yr}^{-1}$ ). The  $^{137}\text{Cs}$  sedimentation rate above the depth of 9 cm was 2.14. This was comparable to the  $^{210}\text{Pb}$  value (Fig. 8). The low  $^{137}\text{Cs}$  sedimentation rate above the depth of 4 cm (Fig. 8) was probably in error due to the upward migration of  $^{137}\text{Cs}$  in the high concentration of organic matter in the surficial sediments of the Crawford Lake core.  $^{137}\text{Cs}$  is adsorbed on fine particles of clay,  $\text{FeS}$ ,  $\text{Fe}(\text{OH})_3$  etc. (Brunskill *et al.*, 1984). The cesium may have become mobile in the pore water of the sediments and moved upcore. This would have resulted in an anomalously low sedimentation rate determination or calculation due to



this upward movement of  $^{137}\text{Cs}$ . A similar phenomenon was observed by Brunskill *et al.* (1984).

With the introduction of reliable dating techniques, i.e.  $^{210}\text{Pb}$ , it is becoming feasible to provide close interval dating of the sedimentary column (Appleby and Oldfield, 1978). This makes it possible to calculate pigments in the accumulating sediment per unit area per unit time, e.g. as amounts of pigment  $\text{cm}^{-2} \text{yr}^{-1}$  (Swain, 1985).

The concentration of chlorophyll derivatives (and some other pigments) can only be used as an index of past production of the lake when a correction is made for the erosion of the organic matter from the surrounding areas of the lake. The processes of soil erosion of pigment-poor organic matter from the catchment of the lake can dilute the concentration of pigments in the sediment core (Sanger, 1988). The calculation of pigment accumulation rates eliminated problems of interpretation owing to dilution.

### **Anaerobic *versus* aerobic sediments**

The results of each downcore pigment profile were shown in the results section for both Crawford Lake and Lady Evelyn Reservoir. Crawford Lake is a meromictic lake with anaerobic conditions in its monimolimnion. Lady Evelyn Reservoir is a dimictic lake which becomes stratified during summers and winters (Ontario Hydro, 1989). The bottom of the hypolimnion of Lady Evelyn Reservoir contained dissolved oxygen at  $4.2 \text{ mg l}^{-1}$  at a depth of 29 m in the summer of 1992 (Dickman and Han, 1992) while no D. O. was present near the bottom of Crawford Lake (Dickman, 1985). Comparing the results of both lakes, we can see that with few exceptions the native chlorophyll was higher and

CD/TC lower in Crawford Lake than in Lady Evelyn Reservoir (Figs. 28 and 29).

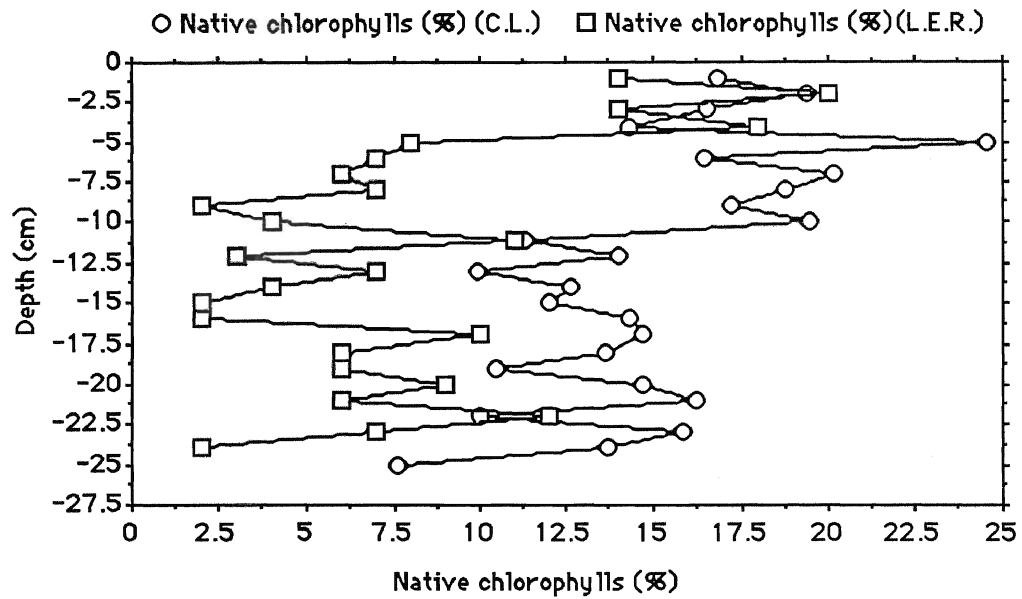


Fig. 28. Comparison of native chlorophylls in Crawford Lake and Lady Evelyn Reservoir.

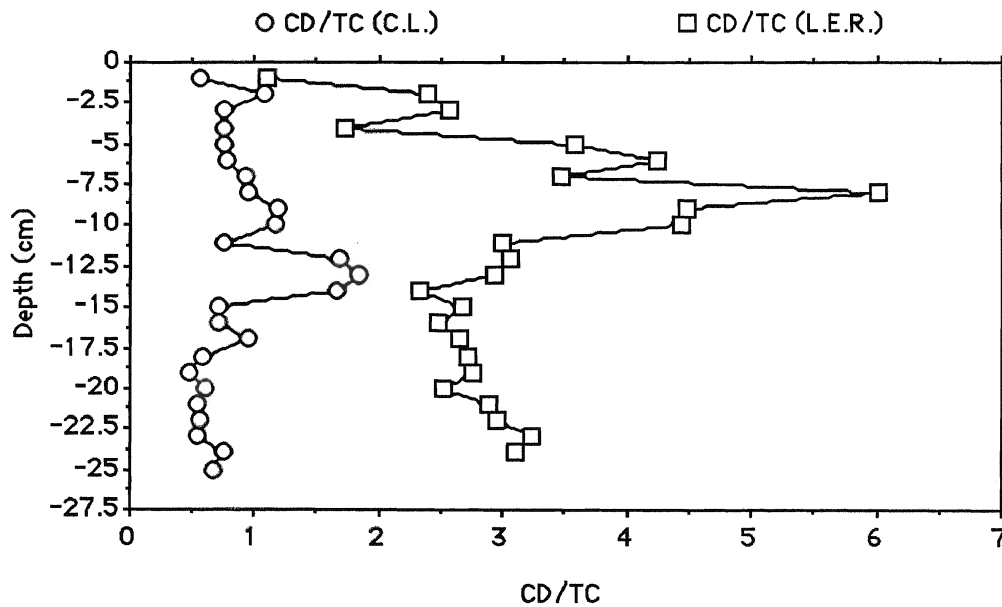


Fig. 29. Comparison of the ratio of chlorophyll derivatives to total carotenoids in Crawford Lake and Lady Evelyn Reservoir.

High native chlorophyll in Lady Evelyn Reservoir was probably caused by high burial rates of pigment-bearing algae due to the high sedimentation rate affected by the dam building and the subsequent acceleration of eutrophication in Lady Evelyn Reservoir.

The native chlorophylls and the ratio of CD/TC can be used as an index of pigment preservation in lakes, i.e. when native chlorophyll is high and CD/TC is low, good preservation has occurred (Swain, 1985). It is believed that under high temperature, high light intensity and high dissolved oxygen, native chlorophyll is readily converted into pheochlorophylls (Sanger, 1988) so that native chlorophyll concentrations become very low in the sediments of lakes with warm well lighted aerobic sediments.

Carotenoids are more likely to decompose under high temperature, intensive light and aerobic conditions than chlorophyll (Gorham and Sanger, 1967) and as a result the CD/TC ratio is high under such conditions. Thus it was no surprise that the concentration of chlorophyll and carotenoids showed higher values in Crawford Lake than in Lady Evelyn Reservoir (Figs. 30 and 31). This good preservation was ascribed to the excellent conditions for pigment preservation in Crawford Lake. The reasons for the better preservation in Crawford Lake were: 1) negligible herbivore grazing (Repeta & Gagosian, 1982; Carpenter & Berquist, 1985). No herbivores occur in the deep sediments of Crawford Lake because the sediments there are anaerobic; 2) photo-oxidation (Welschmeyer & Lorenzen, 1985; Carpenter *et al.*, 1986, 1988) is minimal in Crawford Lake because the phytoplankton and photosynthetic bacteria have very dense populations in the water column especially at 15-16 m (Dickman, 1985). This prevents photooxidation from occurring at 20 m in the bottom sediments; 3) the

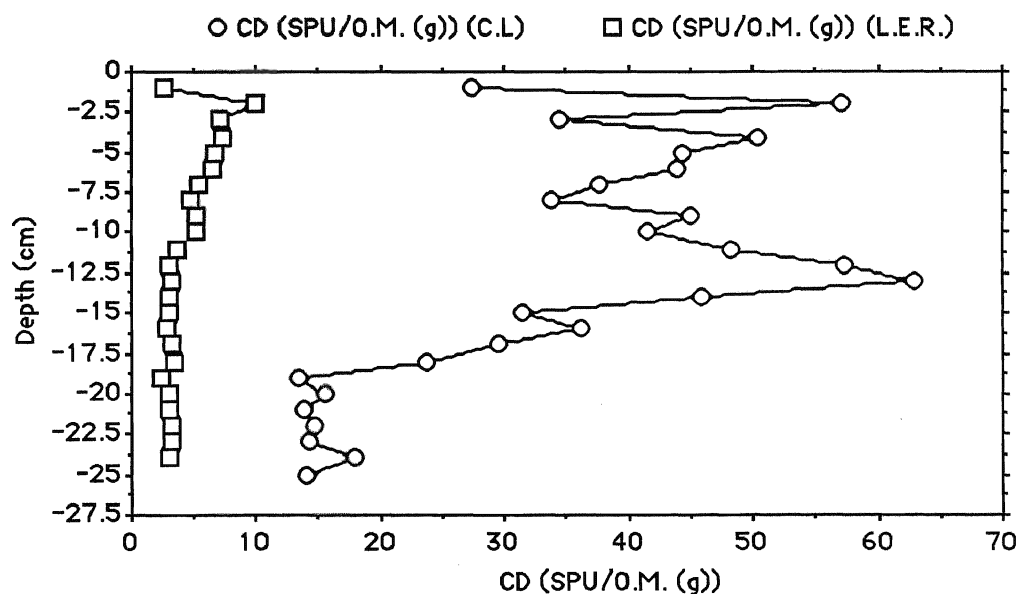


Fig. 30. Comparison of chlorophyll derivatives in Crawford Lake and Lady Evelyn Reservoir

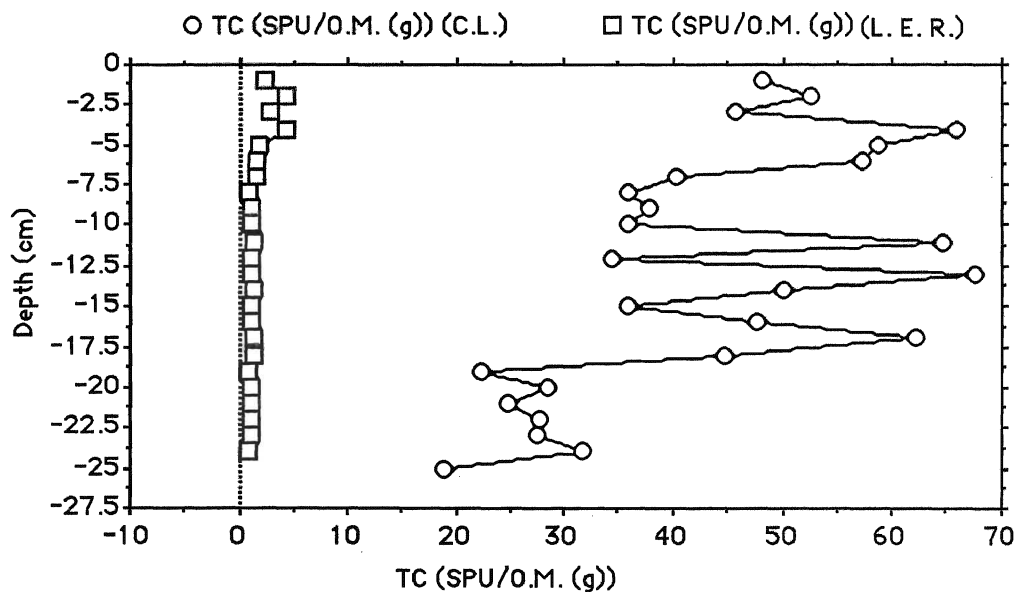


Fig. 31. A comparison of total carotenoids in Crawford Lake and Lady Evelyn Reservoir

temperature (around 6°C) is low in the monimolimnion of Crawford Lake; and 4) a lack of oxygen below 15 m in Crawford Lake prevents the algae from decomposing after they enter this zone.

### **Bacterial degradation of carotenoids in the water column**

The enhancement of pigment degradation by oxygen in the oxic zone of a lake may be a direct chemical action (oxidation) or may be mediated through bacterial processes (increased bacterial metabolism, establishment of different microbial populations) (Leavitt, 1988). Some studies show that highly substituted xanthophyll carotenoids are more labile than carotene pigments (Fogg & Belcher, 1961; Brown, 1969; Zullig, 1982). Myxoxanthophyll is generally more susceptible to degradation than are the other carotenoids (Leavitt, 1988). Because myxoxanthophyll has proven to be a useful paleolimnological indicator of past-blue-green algal populations (Griffiths, 1971; Zullig, 1981; Swain, 1985), such a preferential degradation may lead to the underestimation of the cyanophyte contribution to lacustrine primary production, especially in instances where the surficial sediments are exposed to oxygen or where dead algal cells remain suspended in the oxic zone of the lake for extended periods of time (Leavitt, 1988).

The overall lack of carotenoid degradation under anaerobic conditions has important paleolimnological consequences. Under anaerobic conditions, both the rate and extent of microbially-mediated carotenoid degradation are lower than those of algal organic matter (Leavitt, 1988). The carotenoids were degraded at rates only one-half of those of the algal particulate organic matter under a variety of conditions (Fox *et al.*, 1944; Cranwell, 1976). If oxygen levels are high, as they were in Lady Evelyn Reservoir, the carotenoids degrade faster

than does the total organic matter. As a result, it is not possible to infer the concentration of carotenoids in lakes when dissolved oxygen occurs in the surface sediments. The basis for carotenoid stability is unclear but may be related to the insolubility of the pigments in water (Vallentyne, 1960).

In Crawford Lake, the anaerobic conditions are well established below 16 m (monimolimnion) during the whole year (Dickman, 1985). Under such conditions sedimentary carotenoid levels, expressed as pigment influx, may quantitatively reflect former abundances of photosynthetic organisms which form deep blooms (*Oscillatoriaceae*, and photosynthetic bacteria) or otherwise rapidly sink out of the oxic zone (Leavitt, 1988).

Lady Evelyn Reservoir becomes stratified during the summer. However I speculated that it probably becomes anaerobic only in very late summer (Dickman and Han, 1992). Compared with Crawford Lake, the concentrations of carotenoids including both myxoxanthophyll and total carotenoids in Lady Evelyn Reservoir were very low. This is probably because of poor pigment preservation in Lady Evelyn Reservoir.

### **Bacterial degradation of carotenoids in the sediments**

Although both phytoplankton decay (Depinto, 1977) and pigment degradation (Sanger & Gorham, 1970) occur during algal sedimentation, post-depositional carotenoid diagenesis may also affect fossil carotenoid concentrations (Fogg & Belcher, 1961; Moss, 1968).

Bacterial decomposition of algae affects carotenoid concentrations under experimental conditions (Fox *et al.*, 1944; Cranwell, 1976) and may modify pigment levels in the sediments. Because the temperature of the sediments in Lady Evelyn Reservoir was 7-12 °C (Dickman, 1992)

while in Crawford Lake the 20 m deep sediments were never warmer than 6 °C (Dickman, 1985), it is likely that degradation rates of temperature dependent bacterial decay and direct oxidation are slower in Crawford Lake. Even more important is the fact that the sediments at 20 m in Crawford Lake are permanently anaerobic (Dickman, 1985) and bacterial decomposition in anaerobic sediments is always much slower than in aerobic sediments (Carpenter *et al.*, 1986, 1988).

### Cyanophyte Pigments and Eutrophication

Many reports state that myxoxanthophyll and oscillaxanthin are specific to blue-green algae (Hertzberg *et al.*, 1971). This allows the use of myxoxanthophyll and oscillaxanthin sediment pigment downcore concentrations as an indicator of the relative abundance of blue-green algae in lakes. As cyanophytes (blue-green algae) are generally more common in eutrophic waters (Eberly, 1964; Edmondson, 1968; Griffiths, 1978; Skulberg, 1978; Zullig, 1981, 1986, 1989; Guilizzoni *et al.*, 1983; Engstrom *et al.*, 1985; Rybak and Rybak, 1985; Swain, 1985), it was postulated that these xanthophylls can be used as indicators of lake trophic status (Wetzel, 1983). However, for Crawford Lake, this was not a valid conclusion. The blue-green algae in Crawford Lake were dominated by benthic *Spirulina*, *Lyngbya* and *Oscillatoria* living near the lake's chemocline (Fig. 27). These algae were probably light limited in years when phytoplankton became abundant in the lake (Dickman, pers. comm.). In other words, high accumulation rates of oscillaxanthin in the deep part, i. e. 20-50 cm, in the Crawford Lake core may not indicate eutrophic conditions at that time. Instead, a dense layer of benthic *Lyngbya* and *Oscillatoria* between 12 and 14 m may be the

reason that when phytoplankton was sparse, light intensity at 14 m was high and as a result the benthic *Lyngbya* and *Oscillatoria* density was high. This inverse relationship between phytoplankton pigments and oscillaxanthin in Crawford Lake (Figs. 15 and 23) indicates that the major source of oscillaxanthin is from the benthic algae and not the phytoplankton (Dickman, pers. comm.).

### Identification of the source of organic matter in the sediments by $\delta^{13}\text{C}$ for Crawford Lake

There are potentially three carbon sources in Crawford Lake, i. e. organic matter, atmospheric  $\text{CO}_2$  and carbonates. Organic compounds could be used as carbon sources by bacteria and algae and thus could be important in the regeneration of  $\text{CO}_2$  for photosynthetic growth (Quay *et al.*, 1986). This  $\text{CO}_2$  may be cycled or introduced from organic carbon sources by the breakdown of allochthonous material, dissolved organics, and the decay of autochthonous material (Goldman, 1972).

Blue-green algae are distinguished from other photosynthetic bacteria on the basis of pigmentation and performance of aerobic photosynthesis (Stanier *et al.*, 1971). Blue-green algal blooms occurred only when the pH value was greater than 8.5. Cyanophytes require an elevated pH in order to proliferate (Jackson, 1964). Since at a pH greater than 8.4 very little inorganic carbon is present as  $\text{CO}_2$ , the blue-greens utilize  $\text{HCO}_3^-$  or even  $\text{CO}_3^{2-}$  (Jackson, 1964).

Detrital carbonates may constitute a significant portion of the carbon utilized by the bacteria and algae living in the lake if its drainage basin is underlain by carbonate rocks (Kelts and Hsu, 1978).



### *$\delta^{13}\text{C}$ identification of carbon sources in Crawford Lake*

The source of carbon for bacteria and algal utilization can be indicated by the organic carbon  $\delta^{13}\text{C}$  values in the sediments. The isotopic composition of organic carbon in lake sediments may reflect lake conditions at the time of deposition (Stuiver, 1970). There are two predominant factors influencing the  $^{13}\text{C}$  record, i. e. changes in the organic productivity of a lake and in the hardness of the water (Oana and Deevey 1960; Smith and Epstein, 1971).

The organic fraction of lake sediments is derived from terrestrial plants, plankton, and aquatic macrophytes (Oana and Deevey, 1960). The  $^{13}\text{C}$  contents of terrestrial plants fall into two categories, those with low  $\delta^{13}\text{C}$  values (-24 to -34 ‰) and those with high  $\delta^{13}\text{C}$  values (-6 to -19 ‰) on the PDB - Peedee Belemnite PDB scale (Smith and Epstein, 1971). Floating aquatic plants, utilizing atmospheric  $\text{CO}_2$ , have  $^{13}\text{C}$  ratios similar to terrestrial plants (Oana and Deevey, 1960).

Large changes in  $^{13}\text{C}$  content seem to also be possible for the phytoplankton, depending on the availability of dissolved  $\text{CO}_2$  (Deuser *et al.*, 1968). Maximum fractionation of phytoplankton occurs in hard water lakes. The change in  $^{13}\text{C}$  content of the sediments is consistent with less  $\text{CO}_2$  availability. Another possible mechanism is increased productivity in source water (Stuiver, 1975). Increased organic productivity would raise the  $^{13}\text{C}$  level of the bicarbonate of the water as more organic material deficient in  $^{13}\text{C}$  would have been removed from the source water (Stuiver, 1975).

The main reason for changes in  $^{13}\text{C}$  content of sediments are changes in bicarbonate content of the water. Such a change may cause a shift in absolute  $\delta^{13}\text{C}$  ratio of the carbon reservoir, in addition to a

change in isotope fractionation between plants and bicarbonate. A second mechanism, increased organic productivity resulting in  $^{13}\text{C}$  enriched bicarbonate is also a possible candidate (Stuiver, 1975).

High values of  $\delta^{13}\text{C}$  at the depth of 34-48 cm in Crawford Lake (1480-1760 A. D.) (Fig. 11) were probably caused by blue-green algae, which were the main primary producers living close to the chemocline in the lake. There was a dense population of benthic *Oscillatoriaceae* in the lake during this period. The *Oscillatoriaceae* utilized the bicarbonate, which had a high  $\delta^{13}\text{C}$  value.

The value of  $\delta^{13}\text{C}$  decreased at 19-30 cm. This may have been due to the dilution of the  $^{13}\text{C}$  in the sediments by terrestrial plants with their characteristically low  $\delta^{13}\text{C}$  values.

Very low  $\delta^{13}\text{C}$  values were found at 0-7 cm (Fig. 11). At this time phytoplankton was the main primary producer, which enriched the sediments with  $^{12}\text{C}$  by photosynthetic assimilation.

### **Sediment pigment stratigraphy in Crawford Lake**

The extremely high concentration of oscillaxanthin and myxoxanthophyll at 18-50 cm (1500-1900 A. D.) in Crawford Lake was attributed to the existence of high levels of benthic blue-green algae, e.g. *Oscillatoria*, *Lyngbya* etc. in the lake, and the excellent conditions for xanthophyll preservation (i. e. under low light, low temperature and anaerobic conditions). From 1500 to 1900 A. D., the concentration of chlorophyll derivatives and organic matter content were very low due to dilution by terrestrial organic matter (Figs. 9 and 14). A large portion of CD's were probably brought into the lake by man-induced erosion (Boyko, 1978). After 1900 the chlorophyll derivatives and organic matter dramatically increased due to the acceleration of the

eutrophication process while the blue-green algae at 15 m declined. This may have been due to light inhibition associated with high phytoplankton standing crops.

*Variations of CD and TC related to environmental conditions and sources in Crawford lake*

Chlorophyll derivatives (CD) and total carotenoids (TC) may come from many sources such as aquatic plants, algae, phototrophic bacteria and terrestrial plants (Likens and Bormann, 1974; Gorham and Sanger, 1975; Cotter and Crowl, 1981). For Crawford Lake, Chlorophyll derivatives and total carotenoids were considered to come mainly from aquatic plants, phytoplankton and bacteria. The concentration of chlorophyll derivatives and total carotenoids in the sediments was dominated by several factors: 1) the production of the waters, 2) the influx of terrestrial organic matter, and 3) the sedimentation rate of the organic and inorganic matter in the water column.

The accumulation of CD in lake sediments is often interpreted as being proportional to lake productivity (i.e., lake trophic status) at the time of deposition (Gorham, 1960, 1961; Sanger & Gorham, 1970, 1972; Sanger & Crowl, 1979; Rybak and Rybak, 1985; Rybak, 1986). There are also studies which show that there is a significant positive correlation between profundal concentrations of surface sediment pigments and primary production in lakes (Adams *et al.*, 1978; Gorham, *et al.*, 1974; Guilizzoni *et al.*, 1983). As was noted by Sanger and Crowl (1979) the highest concentration of pigments is observed in meromictic lakes. This is because the reducing environment of the monimolimnion of meromictic lakes preserves the chlorophyll derivatives and other related pigments (Gorham and Sanger 1972).

According to Fjerdingstad (1979) the distribution of different bacterial chlorophylls of the photosynthetic bacteria suggests that bacteriochlorophyll-d (*Chlorobium* chlorophyll-type 650) occurs in most species of the family Chlorobiaceae especially in the genus *Chlorobium*. The family Chlorobiaceae comprises all phototrophic bacteria with green or yellow-green pigment, which develop in environments exposed to light and containing rather high concentrations of hydrogen sulfide (Fjerdingstad, 1979). Hence, the development of bacteria of the genus *Chlorobium* is possible in very specific environmental conditions which occur in meromictic or hypertrophic lakes (Rybak, 1986; Rybak and Dickman, 1988). In addition to the green sulphur bacteria, a few forms of *Chromatium* (a purple sulfur bacterium) were noted at the chemocline of Crawford Lake (Severn, 1981; Dickman, 1985). All purple bacteria (*Chromatium*) contain the same bacteriochlorophyll (Rabinovitz, 1965). The presence of this pigment confers on them the ability to carry out photosynthesis. The primary absorption range of *Chromatium* bacteriochlorophyll in lake water solution is in the range of 770-780 nm (Katz and Wassink, 1939). There are also significant maxima of absorption of this pigment in the shorter wavelength zones around 700, 580-600 and 335-370 nm (Kaplan and Silberman, 1959). Because I did not analyze the sediment samples from Crawford Lake at these longer (770-780 nm) and shorter (335-370 nm) wavelengths, it is likely the *Chromatium* and other purple phototrophic bacteria in the lake were ignored in my sediment pigment analyses. It is also possible the *Chromatium* bacteriochlorophyll was confused with my total chlorophylls. This would explain the near identical downcore profiles of these two pigments (Figs. 14A and 21). Rybak and Dickman (1988) argued that

bacteriochlorophyll and algal chlorophyll concentrations were inversely correlated in a sediment core from Crawford Lake which they felt indicates that when bacteriochlorophyll concentrations were high, algal chlorophyll concentrations were low. They speculated that phytoplankton were outcompeting the photobacteria when nutrients were plentiful in Crawford Lake.

*Temporal variations of accumulation rates of chlorophyll derivatives, total carotenoids, myxoxanthophyll, and oscillaxanthin in Crawford Lake*

Chlorophyll derivatives and total carotenoids both showed high accumulation rates in the upper layer (0-18 cm) of the Crawford Lake core (Figs. 15 and 18). In the same period, the sedimentation rates of organic matter and carbonate content were very high (Figs. 10 and 13). In the profile from Crawford Lake, the accumulation of bacteriochlorophyll-d (Fig. 21) followed closely the accumulation pattern of chlorophyll derivatives as noted above.

It is believed that the carbonates in the sediments of Crawford Lake are composed of two types: 1) primary carbonate (dolomite, calcite, aragonite etc.), and 2) biogenic carbonates. Biogenic carbonates are likely to be the main source of the secondary carbonates found in the sediments of Crawford Lake (Dickman, 1985).

From the profile of myxoxanthophyll (Fig. 25), it was noted that the accumulation of this pigment showed high values during three periods: 1) 1520-1705 A.D., 2) 1860-1905 A.D. and 3) 1955-1978 A.D. There were two possible reasons for this, 1) the increase of loading rates of nutrients and 2) the good preservation of pigments in the Crawford Lake core. During the first two periods, the better

preservation was probably the main reason for the high levels of myxoxanthophyll. At that time, the lake was characterized by low primary production, indicated by a low accumulation rate of chlorophyll derivatives and a low concentration of carbonates which are believed to be of biogenic formation as previously noted. My interpretation of the carbon-13 analyses supports this view.

The main primary producers in Crawford Lake are located at the chemocline between the well lighted mixolimnion and the permanently stagnant and anaerobic monimolimnion (Dickman 1985). A dense population of *Oscillatoria* and *Lyngbya* probably existed on the bottom of the lake above the chemocline during these two periods as indicated by high concentrations of oscillaxanthin and a high ratio of oscillaxanthin to myxoxanthophyll (Fig. 26). As previously noted, good preservation of these blue-green algal pigments led to the high concentration of myxoxanthophyll in the Crawford Lake core (Fig. 25).

#### ***Pigment concentrations related to land use history in the Crawford Lake watershed***

Pollen analysis for the past millenium indicated that Crawford Lake Indians may have cleared and farmed the land around the lake for about 300 years (1310-1610 A. D., Boyko, 1973). The pollen record from Crawford Lake also indicates that before 1471, white pine was unimportant in the surrounding forest and increased due to climatic change and succession on abandoned Indian fields (ibid). As was noted by Boyko (1978) the successive deforestation of the Crawford Lake watershed occurred from 1772 to 1910. The first contractors were authorized to cut lumber for the British Navy in 1772 and after 1826 logging was opened to the public (Boyko 1978). Initially, white oak was

logged, but selective cutting of pine increased after 1812 when Napoleon blocked the British importation of Baltic pine (Ibid).

Soils which were contained by the overlying plant cover, mostly by the forest, became more susceptible to erosion after the felling of the pines (Boyko, 1978). Severe erosion and pine forest clearing was indicated by the many pine needles found in the sediments of the core from 18 to 20 cm. However, pine needles were also abundant below 25 cm and this was attributed to high pine tree densities because pine pollen was also abundant during this same period (Boyko 1978). Above 18 cm pine pollen concentrations were relatively low in the Crawford Lake core (ibid).

From a depth of 18 to 48 cm, oscillaxanthin becomes increasingly abundant in the core (Fig. 23). This was correlated with the period of increased erosion associated with both the felling of the pines and indian farming practices on the shores of the lake (Boyko 1978). I am speculating that during this period erosion carried nutrients into Crawford Lake. These nutrients probably stimulated the growth of *Lyngbya* and *Oscillatoria*, a filamentous cyanobacterium, living on the bottom of the lake near the profundal zone. The reasons for the high density of benthic *Oscillatoriaceae* living near the chemocline during this period are probably: 1) high concentrations of nutrients that were available near the chemocline because of the release of nutrients from the degradation of organisms at the chemocline; 2) high concentrations of  $\text{HCO}_3^-$ , which stimulate blue-green algal abundance (Jackson, 1964); 3) high pH values, which are usually found in hard water lakes (Oana and Deevey, 1960). Ultimately, some of the cyanophytes in the algal mat would have died and released their pigments into the lake's profundal

sediments where low light and anaerobic condition would have resulted in excellent preservation.

The main trophic trend during the period from 1958 to 1978 A. D. was a successive series of increases in the trophic level of Crawford Lake indicating that the lake was undergoing rapid eutrophication (Rybak and Dickman, 1988). The most recent eutrophication process in Crawford Lake (Figs. 15 and 18) was correlated with the fact that in 1969 the property which was privately owned by the Crawford family was sold to the Halton Conservation Authority and a conservation area accessible to large numbers of the public was established. On an average summer weekend, over 1,000 people visit Crawford Lake and many of these use the restroom located above the lake. Because holding tanks and pump out toilets were never installed in the Crawford Lake conservation area it is possible that some of the nutrients from those using the Crawford Lake restrooms, which are perched above the lake, may eventually have found their way into the lake.

The evidence for rapid eutrophication based on increases in the pigments in the sediment core was also supported by evidence from increases in the amount of organic matter (Fig. 10) that was deposited in the bottom of the lake during the same period (1958 to 1978 A. D.). Chlorophyll derivatives, total carotenoids, the amount of organic matter and biogenic carbonate content all increased during this same period (Figs. 10, 13, 15 and 18).



## Conclusions

In order to work out the eutrophication history of Crawford Lake, several kinds of pigments were analyzed. Crawford Lake offers excellent conditions for pigment preservation, reducing problems of differential diagenesis of the pigment molecules, and promoting comparability of the measurements along the length of the sediment core. Although Lady Evelyn Reservoir, a dimictic lake, stratifies in the summer, it becomes anoxic in the bottom water only in late summer. A comparison of the results of pigment preservation in both lakes was one of the goals of my research.

With the introduction of a reliable dating technique -  $^{210}\text{Pb}$  for the core of Crawford Lake, the amount of pigment accumulating in the sediment per unit area per unit time (e.g. as amounts of pigment  $\text{cm}^{-2} \text{yr}^{-1}$ ) was calculated. The calculation of pigment accumulation rates eliminated problems of interpretation due to dilution.

By using the results of organic carbon  $\delta^{13}\text{C}$  in the sediments of Crawford Lake, different sources of organic matter in the sediments could be distinguished.

This research proved that native chlorophyll can be used to indicate the condition of pigment preservation in both Crawford Lake and Lady Evelyn Reservoir. Native chlorophyll was collectively affected by temperature, light intensity, oxidation conditions and burial rate (related to sedimentation rate). The CD/TC ratio varied with sediment pigment preservation characteristics due to the different degradation rates of chlorophyll and carotenoids. Both of these indicators, native chlorophyll and the CD/TC ratio, supported the view that Crawford Lake

has a better pigment preservation environment than Lady Evelyn Reservoir.

In Crawford Lake, the anaerobic conditions result in a very low decomposition rate of carotenoids, especially highly substituted xanthophyll carotenoids, such as oscillaxanthin and myxoxanthophyll. The concentrations of oscillaxanthin and myxoxanthophyll, both of which are expressed as micrograms per unit gram organic matter, are extremely high in Crawford Lake compared with those in Lady Evelyn Reservoir.

It is widely accepted that the concentration or accumulation rate of blue-green algal pigments, e.g. oscillaxanthin and myxoxanthophyll, can be used as indicators of lake eutrophication, (i.e. they are higher in eutrophic lakes than in oligotrophic lakes). In other words, the accumulation rates of these pigments can indicate the trophic levels of a lake. However, this is not true in Crawford Lake. High accumulation rates of oscillaxanthin and myxoxanthophyll in the deep part of the sediment core in Crawford Lake (20-50 cm, 1480-1900 A. D.) may not indicate eutrophic condition at that time. Instead, a dense layer of benthic *Lyngbya* and *Oscillatoria* living on the bottom of the lake between 12 and 14 m may be the reason for the presence of these pigments at elevated levels in the Crawford Lake core. This hypothesis is supported with the following evidence:

- 1) The accumulation rates of oscillaxanthin and myxoxanthophyll show an inverse relationship with those of CD, TC and organic matter in Crawford Lake (Figs. 10, 15, 18, 23 and 25). This is likely the result of competition for light between phytoplankton and benthic blue-green algae. From 1955 to the present, Crawford Lake became more and more eutrophic. During this period, the accumulation rates of CD, TC and

organic matter were very high, and the accumulation rates of cyanophyte pigments during this period were very low (Figs. 10, 15, 18, 23 and 25).

2) Benthic cyanophytes utilize  $\text{HCO}_3^-$  or even  $\text{CO}_3^{2-}$  for photosynthetic reactions (Jackson, 1964). In Crawford Lake, the pH values near the chemocline range from 8.2 to 8.6 (Dickman, pers. comm.) and the concentration of detrital carbonates (its drainage basin is underlain by carbonate rocks) is high. High values of organic carbon  $\delta^{13}\text{C}$  were found at 34-48 cm (1480-1760 A. D.) (Fig. 11). This was probably caused by the high density of blue-green algae living close to the chemocline in the lake. Very low values of organic carbon  $\delta^{13}\text{C}$  at 0-7 cm was probably due to elevated levels of phytoplankton at this time (1955-present).

The environmental changes which have occurred in Crawford Lake from 1480 A. D. to the present are summarized by the following:

#### ***1480 - 1760 A. D.***

During this period, Crawford Lake Indians cleared and farmed the land. This caused some allochthonous organic matter and detrital carbonates to enter the lake. The degradation of the organic matter released  $\text{CO}_2$  dissolving some of the detrital carbonates. The nutrient release and the formation of bicarbonates stimulated blue-green algae to proliferate (Stanier *et al.*, 1971). How many of these were benthic algae and how many were phytoplankton is not known.

Before 1480 A. D., the lake was characterized by low primary production which was indicated by the low accumulation rate of chlorophyll (Fig. 15). The main primary producers in the lake were probably located at the chemocline where bicarbonate and phosphorus

were more available. There appears to have been a dense population of *Oscillatoria* and *Lyngbya* near the chemocline (Fig. 27) as inferred from the relatively high organic carbon  $\delta^{13}\text{C}$  values (Fig. 11) and the extremely high accumulation rates of oscillaxanthin at 33-48 cm (1480 - 1760 A. D.) (Fig. 23).

#### **1760 - 1900 A. D.**

Europeans began to colonize the Crawford Lake watershed during this period. The major deforestation of Crawford Lake occurred after 1772 A. D. (Boyko, 1978). The first contractors were authorized to cut lumber for the British Navy in 1772 and after 1826 logging was opened up to the public. The land clearance caused severe erosion. The loading rate of nutrients and detrital carbonates probably increased to the lake during this stage. Although this increased primary production, the poor pigment-containing allochthonous organic matter would have diluted the autochthonous organic matter entering the monimolimnetic waters. The accumulation rate of chlorophyll remained high (Fig. 15). The organic carbon  $\delta^{13}\text{C}$  decreased (Fig. 11) because of its dilution by terrestrial plant inputs. The carbonate content of the sediments increased (Fig. 10) due to inputs of both biogenic carbonates formation and erosion of detrital carbonates.

#### **1899 - 1955 A. D.**

The Crawford family operated a shingle-mill from 1899-1929 A. D., which was located at the southern end of the lake (Boyko, 1978). This resulted in a lot of organic carbon and nutrients entering the lake. As a result, the primary productivity of the lake increased,

which was indicated by high accumulation rates of pine needles and chlorophyll derivatives (Fig. 15).

From 1899 to 1955 A. D. a transition period occurred in which benthic algae such as the deep dwelling *Oscillatoria* and *Lyngbya* declined and phytoplankton abundance increased (Figs. 15, 18, 23 and 25).

### **1955 - 1992 A. D.**

The main trophic trend during the period from 1955 to 1992 A. D. can be described as successively increasing levels of lake eutrophication. During this period, phytoplankton pigments accumulated at high rates while benthic Cyanophyte pigments declined (Figs. 15, 18, 23 and 25).

Urban development, farming and especially reforestation were observed during this period (Boyko, 1978). In 1969 the property which belonged to the Crawford family was sold to the Halton County Conservation Authority and a conservation area was established. The observed acceleration in the successive eutrophication process in the lake was most evident after 1969.

In conclusion, the use of palaeopigments in combination with organic carbon stable isotopes permits intelligent inferences of palaeoproductivity in both meromictic and dimictic lakes in Central Canada. It is believed that similar technique will prove applicable throughout the northern hemisphere.

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